Application of a layered triangular-lattice magnetic model system to LiNiO$_2$

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The magnetic susceptibility of LiNiO$_2$ can be described by a high-temperature Curie-Weiss law that is typical of ferromagnets but without spontaneous magnetization at low temperatures. We find that some of the ESR features of LiNiO$_2$ below 40 K which were earlier attributed to a quantum spin-liquid state are present at higher temperatures around 240 K in Li$_{0.3}$Ni$_{0.7}$O. This behavior is typical of superparamagnetic domains. The magnitude of the ^{7}Li NMR anisotropic paramagnetic dipolar shift in La$_2$Li$_{0.5}$Ni$_{0.5}$O$_4$ and LiNiO$_2$ suggests that the moment is localized predominantly on Ni ions. Arguments are presented to suggest that the systematics are consistent with the predominant creation of holes on Ni on the substitution of Ni by Li in NiO. The same conclusion is drawn from the ESR studies.

I. INTRODUCTION

Interest in LiNiO$_2$ as a model for a frustrated antiferromagnetic triangular lattice has been stimulated mainly through the efforts of Hirakawa and co-workers.[1-3] Yamada *et al.*[2] attempted to characterize the system further by electron spin resonance (ESR) studies. A minimum in the resonance linewidth at T_{N1}, splitting of the line at low temperatures as well as large changes in the resonance field (becoming even negative) and linewidth of these signals with low temperatures characterized the system and was attributed to the spin-liquid state discussed for triangular lattice systems by Anderson.[4,5]

There are two crucial assumptions in this model. The first of these is that the magnetic moments are located on the Ni^{3+} ions and that the predominant magnetic interactions are antiferromagnetic because of the presence of high-temperature antiferromagnetism in the parent NiO with 180° Ni-O-Ni interactions. In addition, the magnetic moment is expected to be present on the Ni ion. In the idealized structure of LiMO$_2$ there exist only 90° M-O-M interactions which favor ferromagnetic ground states[6,7] because of the involvement of orthogonal orbitals.[8]

Recently, the stability of a Ni^{3+} oxidation state in an oxide matrix has been questioned. Ganguly and co-workers[9,10] suggested that the Ni^{3+} level is located in the valence band of anionic character and this could create holes in the oxygen ions by charge transfer from the oxygen (O^{2-}) ions to the Ni^{3+} ions. Kuiper *et al.*[11] have more recently suggested from x-ray O K-edge studies that the holes are located predominantly on oxygen. In this case the very character (both geometrical and magnetic) of the layered lattice structure is open to question. The hexagonal-close-packed character of the oxygen ions now gives rise to a triangular lattice. When the moment is on oxygen, the ions may interact antiferromagnetically with one another, leading to a singlet "peroxide"-like moiety.[9,10,12]

In this paper we report the results of our investigations on Li$_x$Ni$_{1-x}$O and LiCo$_x$Ni$_{1-x}$O$_2$. We find that the magnetic susceptibility behavior of LiNiO$_2$ is very close to what seems to be a general behavior of layered oxides in which the high-temperature Curie-Weiss law that is typical of ferromagnets does not result in a ground state with long-range ferromagnetic order with a spontaneous magnetization. We have reexamined the ESR signal and find that some of the ESR features of LiNiO$_2$ below 40 K which were attributed earlier to a quantum spin-liquid state is present at higher temperatures around 240 K in Li$_{0.3}$Ni$_{0.7}$O. This behavior is consistent with the existence of a superparamagnetic state. The magnitude of the ^{7}Li NMR anisotropic paramagnetic dipolar shift in La$_2$Li$_{0.5}$Ni$_{0.5}$O$_4$ and LiNiO$_2$ suggests that the moment is localized predominantly on Ni ions. Arguments are presented to suggest that the systematics are consistent with the predominant creation of holes on Ni on the substitution of Ni by Li in NiO. The same conclusion is drawn from the ESR studies. If, at all, there is a creation of holes on oxygen in LiNiO$_2$, it is not accompanied by the creation of a spin on oxygen.

II. EXPERIMENT

The compounds were prepared by the standard ceramic method using Li$_2$CO$_3$ and nickel or cobalt oxalate as starting material. Required stoichiometric amounts of the starting materials were weighed out and ground under alcohol for several hours. The dried mixture was then prefired in air at 600 °C for 6 h. The prefired product was then pelletized and fired in oxygen at 820 °C for 16 h with intermittant grinding and pelletizing.

Room-temperature x-ray diffraction patterns were recorded on a Philips 1730 machine using Cu K radiation. All the lines were indexed on the basis of a single unit cell. An estimation of the amount of lithium that is present was done by matching the observed with the simulated powder pattern by refining the occupation

numbers of the positional coordinates of the various metal ions. The ESR spectra were recorded on a Bruker ER 200D–SRC electron spin resonance spectrometer capable of operating between 300 and 160 K. The magnetic-susceptibility measurements were performed by the standard Faraday method using a CAHN electrobalance.

Lithium NMR experiments were carried out on a Bruker MSL 300 FT-NMR spectrometer operating at a magnetic field of 7 T. For ^{7}Li NMR observation at 116.64 MHz the probe had to be retuned with additional circuitry. In the single-pulse-sequence experiments carried out for this work, a single, nonselective pulse with a preacquisition delay of 4 μs was employed. Free-induction decays were collected in quadrature channels of a Bruker BC-131 digitizer and standard phase cycling into the pulse sequence was incorporated to minimize artifacts in the receiver. Magic-angle sample-spinning (MAS) spectroscopy was carried out at two spinning speeds of 4.3 and 3.2 kHz. The magic angle was precisely adjusted using a KBr sample.

III. RESULTS AND DISCUSSION

A. Structural parameters

The lattice parameters of some of the important compositions studied in this paper are given in Table I. We were not able to obtain stoichiometric $LiNiO_2$. Our best sample had the composition $Li_{0.48}Ni_{0.52}O$.

The variation of the pseudocubic a parameter is fairly linear with x for the series $Li_xNi_{1-x}O$ until $x \simeq 0.3$. There is a deviation from Vegard's law around $x \simeq 0.3$ in this study which has been observed in earlier studies[13] indicating improper solid solution formation. The refinement of the positional and site-occupation parameter of $Li_{0.3}Ni_{0.7}O$ has been carried out (Table II). It was found that the intensities of the diffraction lines are consistent with the $LiNiO_2$ structure in which two-thirds of

the Li sites are occupied by Ni, and one-third of the Ni sites are occupied by Li ions. These results are consistent with the existence of a layer sequence $(LiO)^-(NiO)_2^+$ with two hexagonal NiO layers adjacent to each other. Thus, we shall term the $x = 0.3$ composition as the "$LiNi_2O_3$" phase. The deviation from Vegard's law for $x \geq 0.3$ may indicate, therefore, a solid solution instability with perhaps the coexistence of $LiNi_2O_3$ and $LiNiO_2$.[14]

B. Magnetic-susceptibility studies

The magnetic-susceptibility behavior of the $x = 0.3$, 0.46, and 0.48 compositions of $Li_xNi_{1-x}O$ is shown in Fig. 1. $LiNi_2O_3$ shows an abrupt increase in the susceptibility between 260 and 230 K. Below 230 K the susceptibility is quite independent of temperature. The ESR results (to be discussed later) suggest that the behavior at 230 K is associated with a genuine phase transition. The $x = 0.48$ and $x = 0.46$ samples show Curie-Weiss behavior (see Fig. 1) at high temperature typical of ferromagnets. We obtain a Curie constant close to 0.37 emu/K for the $x = 0.48$ composition, which is the value of the Curie constant for a single unpaired electron and is consistent with the existence of a low-spin Ni^{3+} ion. The paramagnetic Curie temperature Θ as well as the magnetic susceptibility is found to be lower in the $x = 0.48$ composition. The decrease in Θ with improved stoichiometry is consistent with the recent results of Kemp *et al.*[7] In accordance with the findings of Kemp *et al.*[7] we find that the extrapolated value of the spontaneous magnetization at the lowest temperatures (obtained from the magnetization versus field plots) decreases as the stoichiometric composition is approached.

We have carried out magnetic susceptibility studies on $LiCo_xNi_{1-x}O_2$. Since $LiCoO_2$ is diamagnetic the contribution to the susceptibility is from the Ni ions. The value of Θ increases with x in this series. For all values of x the Curie constant per gram atom of Ni ions is close to 0.37 emu/K.

The ferromagnetic interaction inferred from the high-temperature susceptibility between low-spin Ni^{3+} ions in the $LiNiO_2$ matrix is entirely consistent with the Goodenough-Anderson superexchange rules.[4,6,7] The nearest-neighbor Ni ions are linked through 90° Ni-O-Ni linkages so that the nickel-nickel exchange interactions involve orthogonal oxygen p orbitals favoring thereby the ferromagnetic ground state. In a ferromagnetic ground state there is no frustration and the question of the existence of a quantum liquid-spin state associated with frustrated triangular lattices does not arise. Antiferromagnetic interactions, if at all present in $LiNiO_2$, could then arise only from direct cation-cation interactions. These latter interactions are not known to influence to any significant extent the magnetic properties[6] of the late $3d$ transition metal monoxides.

The absence of spontaneous magnetization at low temperatures, despite a high-temperature Curie-Weiss is one of the remarkable features of layered perovskite oxide systems.[15–17] The origin of this behavior is not clear and may be rationalized[15] by magnetocrystalline anisotropy arguments with the easy axis of magnetization being per-

TABLE I. The variation of the lattice parameters as a function of x in $Li_xNi_{1-x}O$ samples.

Composition	Lattice parameter[a] (Å)	
	$a_h (a_{Rh})$	$c_h (\alpha_{Rh})$
$Li_{0.1}Ni_{0.9}O$	4.156	
$Li_{0.2}Ni_{0.8}O$	4.14	
$Li_{0.3}Ni_{0.7}O$	2.911	14.254
	(5.04)	(33°34′)
$Li_{0.33}Ni_{0.67}O$	2.899	14.2076
	(5.0229)	(33°32′)
$Li_{0.39}Ni_{0.61}O$	2.899	14.2101
	(5.0237)	(33°32′)
$Li_{0.41}Ni_{0.59}O$	2.889	14.197
	(5.018)	(33°28′)
$Li_{0.44}Ni_{0.56}O$	2.888	14.197
	(5.018)	(33°27′)
$Li_{0.46}Ni_{0.54}O$	2.886	14.187
	(5.014)	(33°27′)
$Li_{0.48}Ni_{0.52}O$	2.888	14.19
	(5.015)	(33°28′)

[a]Values in the parentheses are for a rhombohedral cell.

TABLE II. Comparison of observed and calculated intensities of $Li_xNi_{1-x}O$ samples. Intensities were calculated for various occupations of the Li and Ni sites in $LiNiO_2$, space group $R\bar{3}m$ as indicated in bottom of table.

Observed			h	k	l	Calculated	Intensity	
2Θ	Intensity	2Θ		hex		case I	case II	case III
18.8	2.2	18.69	0	0	3	31.5	0.0	2.4
		36.16	1	0	1	14.8		1.0
37.9	42.2	37.84	1	1	2	47.7	47.7	42.2
			0	0	6			
44.0	100.0	43.98	1	0	4	100.0	100.0	100.0
		48.15	1	1	5	5.6		0.4
		58.20	1	0	7	3.7		0.3
			0	0	9			
63.95	43.3	63.92	2	1	0	44.1	44.1	43.9
64.1	28.3	64.06	1	1	0	26.8	26.8	26.6
		67.20	1	2	3	3.2		0.2
		67.40	2	1	3	1.8		0.1
		75.69	2	0	1	0.6		0.1
76.7	11.7	76.73	2	1	6	14.0	14.0	12.8
			1	2	6			
			1	0	10			
80.8	11.1	80.83	0	0	12	6.1	11.4	11.3
			2	−2	4			

		Occupancy (%)		
Ion	Site	case I	case II	case III
Li	1a	60	30	43
Ni	1a	40	70	57
Li	1b	0	30	28
Ni	1b	100	70	72
O	2c	100	100	100

pendicular to the plane. This behavior is found only for the single-layered perovskite oxide system. Halides with related structures such as K_2CuF_4 or Rb_2CrCl_4 show a well-defined ferromagnetic behavior below an ordering temperature.[18,19] Even in the layered oxides, two layers
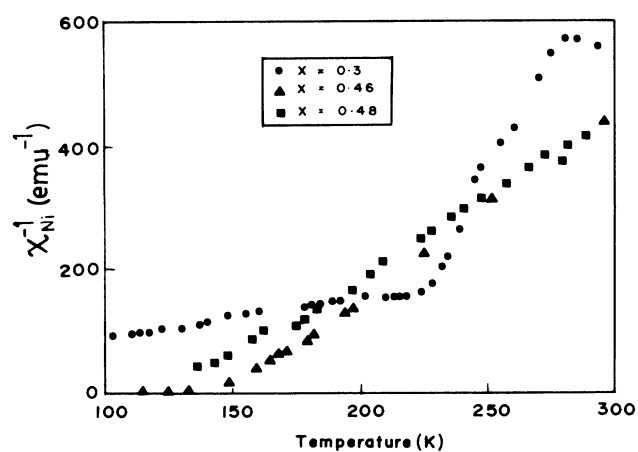

FIG. 1. Inverse magnetic susceptibility per g atom of Ni(X_{Ni}^{-1}) vs temperature plot of the $x = 0.3$, 0.46, and 0.48 compositions.

are sufficient to show spontaneous magnetization and the full three-dimensional behavior is recovered in a triple perovskite layered system.[16] When $x < 5.0$, there are likely to be some Ni ions in the LiO layers which give rise to a stronger exchange coupling between the layers. Thus, the existence of interlayer 180° Ni-O-Ni interactions in the $x \simeq 0.5$ composition may be responsible for enhancing the magnetic susceptibility and introducing spontaneous magnetization.

In $LiNi_2O_3$ ($x \simeq 0.3$ with the postulated -LiO-NiO-NiO-LiO-layered structure) the coupling between the two adjacent NiO layers involves 180° Ni-O-Ni interactions which are expected to be antiferromagnetic. Thus, although there may be a ferromagnetic polarization of the spins in one -NiO- layer due to 90° intralayer Ni-O-Ni interactions, there may not be a spontaneous magnetization because of the antiferromagnetic interlayer 180° Ni-O-Ni interactions. Antiferromagnetic coupling between the layers could give a ferrimagnetic behavior when there is some segregation of Ni^{2+} and Ni^{3+} spin states in different layers. The ferrimagnetic nature of the inverse susceptibility versus temperature plot (Fig. 1) may suggest such a segregation. The extent of such a segregation is likely to be small. The absence of a spontaneous magnetization suggests that the same mechanism of suppression of spontaneous magnetization in layered *ferromagnetic* oxide systems is also operative in layered *ferrimagnetic* oxide systems.

C. Electron-spin-resonance studies

The ESR signal from $LiCo_{0.95}Ni_{0.05}O_2$ in which the Ni ions are isolated from one another is $\simeq 2.10$ and is nearly the same as that reported by Yamada *et al.*[2] for $LiNiO_2$. We have observed that the g value is independent of x in $LiCo_xNi_{1-x}O_2$. The g value of 2.1 is the average[20] g value of the ESR signal from $La_2Li_{0.5}Ni_{0.5}O_4$ in which the $g_{\parallel}$ and $g_{\perp}$ components are clearly seen. The same g value is observed for the ESR signal for Ni^{3+} ions substituted in a small amount in $LaAlO_3$. The $g = 2.1$ of the Ni^{3+} ion, compared to the high g value ($\sim 2.3 - 2.5$) in the fluorides,[21] is due to the strong hybridization with the ligand oxygens. The value of $g \sim 2.1$ for Ni^{3+} ions in the oxides, compared to $g \sim 2.3 - 2.5$ in fluorides, suggests that the spin is mainly centered on the metal and not on the ligand. The ESR signal from isolated O^- ions has a g value close to 2.0.[22]

The temperature dependence of the ESR spectra from $LiNi_2O_3$ is shown in Fig. 2. The ESR spectra are broad and Gaussian in nature with $g = 2.1$ at 300 K. With a decrease in temperature the line narrows considerably and develops a Lorentzian line shape. At ~ 260 K the nearly symmetric ESR line develops in asymmetry which increases with decreasing temperature, indicating the appearance of a new signal. At ~ 238 K the splitting into two signals (designated as A and B) is clearly visible. The
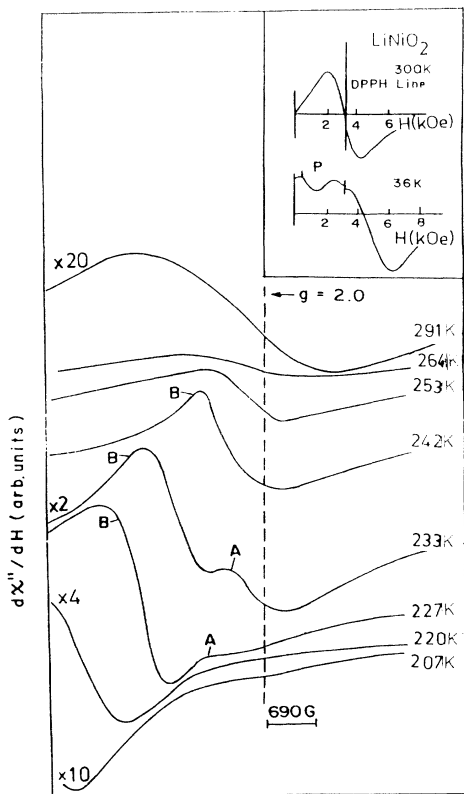
line at higher fields (line A) has a g value of 2.1, indicating that the high-field signal corresponds to the species present at room temperature. The intensity of the line A, I_A, goes through a maximum at ~ 260 K and becomes zero at ~ 230 K [Fig. 3(a)]. The width of the line A, W_A, decreases linearly with temperature and extrapolates to zero width at 230 K [Fig. 3(b)]. The magnetic field position at resonance, H_B, of the new line (line B) decreases very rapidly below 240 K and becomes negative below 210 K [Fig. 3(c)]. The behavior of this line B at lower temperatures is similar to that of the additional line in $LiNiO_2$ observed by Yamada *et al.*[2] below 40 K (their line P; see inset of Fig. 2). Yamada *et al.*[2] attribute this behavior to the formation of a quantum spin-liquid state of a triangular antiferromagnetic lattice. On the other hand, the onset of this behavior in the "$LiNi_2O_3$" is to be associated with the end of the "ferrimagnetic" transition seen in the magnetic susceptibility (Fig. 1) which we have suggested is associated with the onset of antiferromagnetic coupling through $180°$ Ni-O-Ni interactions. The results of Yamada *et al.*[2] as well as those obtained by us bear a striking resemblance to the ESR signals obtained, for example, by Sharma and Baiker[23] from superparamagnetic Ni particles. Thus, the temperature depen-
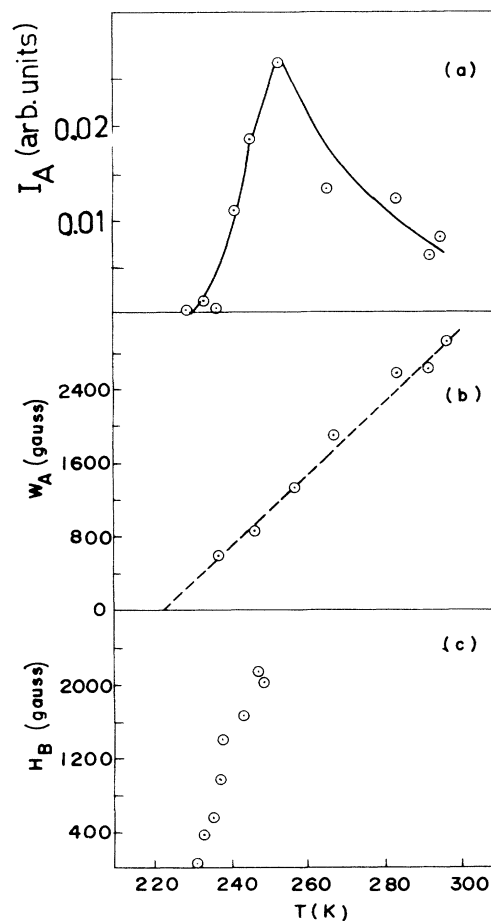

FIG. 2. ESR spectra from $Li_{0.3}Ni_{0.7}O$ as recorded at different temperatures. The lines A are the high-field signal corresponding to the species present at room temperature and line B is the new line that appears on lowering the temperature. Inset shows the ESR spectra from literature (Ref. 2).

FIG. 3. (a) Intensity I_A of line A; (b) changes in linewidth, W_A, of line A, and (c) resonance field position, H_B of line B in $Li_{0.3}Ni_{0.7}O$.

dence of the ESR signals observed with $LiNi_2O_3$ by ourselves and Yamada et al.[2] could thus arise from a superparamagnetic state in which the system is broken up into small ferromagnetic domains suppressing, thereby, any spontaneous magnetization. The creation of superparamagnetic domains is consistent with the mechanism of suppression of spontaneous magnetization[15] in layered oxides due to the orientation of the easy axis of magnetization perpendicular to the plane of two-dimensional magnets.

D. ^7Li NMR studies

The ^7Li NMR study has been carried out to examine the location of the moments associated with the holes by examining the paramagnetic shift due to the dipolar fields in these magnetically anisotropic systems. The ^7Li NMR line is narrow in the nonmagnetic compounds containing only Co ions as in $LiCoO_2$ and $La_2Li_{0.5}Co_{0.5}O_4$ (see Fig. 4).

The replacement of Co^{3+} ions by Ni^{3+} ions in both compounds leads to a large shift in the position (s_c) of the central transition. δ_c in $LiNiO_2$ (~ 580 ppm) is more than ten times that in $La_2Li_{0.5}Ni_{0.5}O_4$ (~ 40 ppm, isotropic line position obtained from MAS). These results are in agreement, respectively, with those of Itoh et al.[3] and Villeneuve et al.[24] δ_c is expected to be mainly due to a dipolar field, H_D, as in these anisotropic systems the dipolar field does not go to zero. The dipolar field is given by

$$H_D = (1/r_i^3)(\mathbf{m} - r_i\mathbf{r}_i \cdot \mathbf{m}_i/r_i^2) ,$$

where $\mathbf{m}_i$ is the magnetic moment at the ith site magnetic site. The magnetic site could be the Ni site or the oxide ions if a hole on oxygen is also associated with a spin. Taking into account the enhancement of the moments
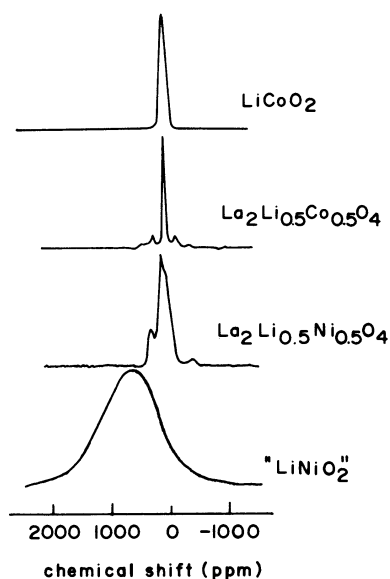
due to ferromagnetic interactions between the Ni ions, the calculated dipolar shift in $LiNiO_2$ when the moment is on the Ni ions is 6–8 times larger than that in $La_2Li_{0.5}Ni_{0.5}O_4$. This is more in agreement with our experimental results. Itoh et al.[3] also found good agreement with experimental results when the dipolar shift is calculated, assuming that the spins are on the Ni ions. Thus, the NMR results show that even if a hole is created on oxygen the moment remains on the Ni ions.

These results may be examined in the context of the recent results of Kuiper et al.[11] who show evidence for holes on oxygen from oxygen K-edge x-ray absorption spectroscopy. The creation of a hole on oxygen is according to the reaction

$$Ni^{3+}(\text{low spin, } t_{2g}^6, e_g^1) + O^{2-} \leftrightarrow Ni^{2+} (\text{low spin}) + O^- .$$
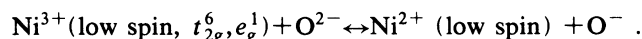
In the charge-transfer process the paired state of the electrons on the diamagnetic precursor O^{2-} ion is unaffected as a consequence of spin-conservation constraints. Kuiper et al. have also argued that the spins on the holes on oxygen are strongly coupled antiferromagnetically to another spin (actually the transferred ligand electron) in the Ni^{2+} $3d^8$ manifold electron. The magnetic state and the magnetic properties are thus essentially determined by the electronic configuration of the precursor metal state. This is shown in Fig. 5 for an initial low-spin Ni^{3+} state [Fig. 5(a)] or a high-spin state [Fig. 5(d)]. The Ni^{2+} ion is in the low-spin state [Fig. 5(b)] requiring a lattice distortion to lift the degeneracy of the e_g orbitals (as in $La_2Li_{0.5}Ni_{0.5}O_4$). It can be seen from Figs. 5(b) and 5(d) that the charge transfer is accompanied by the creation of spins on the oxygen ligand although these spins are always coupled antiferromagnetically to the spin of the transferred electron. In Fig. 5(c) the Ni^{2+} ion is in the high spin with degenerate e_g orbitals consistent with the

FIG. 4. ^7Li NMR spectra obtained from (a) $LiCoO_2$, $La_2Li_{0.5}Co_{0.5}O_4$, $La_2Li_{0.5}Ni_{0.5}O_4$, and $LiNiO_2$ ($Li_{0.46}Ni_{0.54}O_2$).
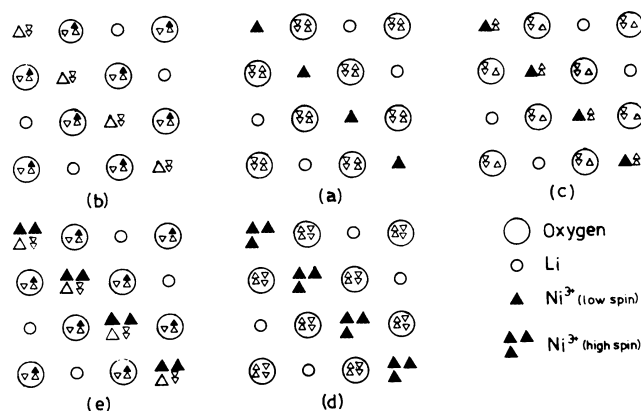
FIG. 5. Possible spin configuration before and after charge-transfer from ligand to Ni^{3+} ion. Each spin on the ligand oxygens is schematically shown by a pair of small triangles representing contributions from the two p orbitals involved in this diagram. In the metal each electron spin state is shown by the large triangle. Unpaired electrons or electrons contributing to the total spin of the system are shown by filled triangles. (a) and (d) correspond to configurations for the initial states for low-spin and high-spin Ni^{3+} ions.

cubic symmetry of the NiO_6 octahedra in these compounds. Magnetic-susceptibility studies are consistent with a low-spin configuration. Our NMR results on $LiNiO_2$ are consistent with a dominant contribution from the initial-state configuration of Fig. 5(a) and the final-state configuration of Fig. 5(c), involving the moments on low-spin Ni^{3+} ions. The ESR g values also support this conclusion.

It would seem that the g value of the ESR signal as well as the magnitude of the dipolar shift in $La_2Li_{0.5}Ni_{0.5}O_4$ can only be consistent with the absence of a charge transfer from ligand to Ni or the creation of a hole on oxygen. This is based on the assumption that the crystal field in $La_2Li_{0.5}Ni_{0.5}O_4$ lifts the degeneracy of the e_g orbitals as in Fig. 5(b), which is consistent with the anisotropic g values of its ESR signal.

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