Structural effects in the EPR spectra of Ni$^{3+}$ in La$_2$Ni$_{0.5}$Li$_{0.5}$O$_4$

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Electron paramagnetic resonance (EPR), Raman scattering, and neutron- and x-ray-diffraction experiments were performed in polycrystalline samples of La$_2$Ni$_{0.5}$Li$_{0.5}$O$_4$ as a function of temperature. Structural studies confirm a partial cation ordering of Ni and Li at the metal sites. As the temperature decreases, EPR measurements show an increasing g-value anisotropy ($g_{eff} - g_{||}$) and neutron and x-ray-diffraction experiments an increase of the $c/a$ ratio. These results are interpreted in terms of the stabilization of the Ni$^{3+}$(3$d^7$)$^2$A$_{1g}$ low-spin configuration in the NiO$_6$ Jahn-Teller distorted octahedra.

I. INTRODUCTION

The study of the physical and structural properties of oxides of K$_2$NiF$_4$-type structure has been a subject of great interest in the last decade due to the discovery of high-$T_c$ superconductivity in the La$_{1.85}$Sr$_{0.15}$CuO$_4$ cuprate. In the stoichiometric La$_2$NiO$_4$, the Ni ions form a spin-1 sublattice rather than a spin-1/2 sublattice as in the cuprates. The La$_2$NiO$_{4+\delta}$ compound can be synthesized in a broad range of nonstoichiometric oxygen content (0 $\leq$ $\delta$ $\leq$ 0.25), with structural, electric, and magnetic properties highly dependent on $\delta$.

The presence of extra oxygen ions yields to $p$-type doped NiO$_2$ layers alternating with rocksalt-type La$_2$O$_2$+$\delta$ layers of variable oxygen content. Moreover, in the attempt to observe high-$T_c$ superconductivity in the nickelates, Sr and Li hole-doped La$_{2-x}$Sr$_x$NiO$_{4+\delta}$ and La$_2$Ni$_{1-x}$Li$_x$O$_4$ compounds were synthesized. However, these materials do not superconduct for any value of $x$ and $\delta$. Moreover, no appreciable Li losses were observed in our specimens. Neutron and x-ray powder diffraction revealed that the data can be interpreted in terms of a further stabilization of the Ni$^{3+}$(3$d^7$)$^2$A$_{1g}$ low-spin configuration in La$_2$Ni$_{0.5}$Li$_{0.5}$O$_4$ at low $T$.

II. EXPERIMENTAL DETAILS

The polycrystalline samples studied in this work were synthesized using a standard ceramic preparation method. The corresponding stoichiometric amounts of La$_2$O$_3$, NiO, and Li$_2$CO$_3$ were mixed and fired at 900 °C over a multiday period with several intermediate regrindings. The rather low sintering temperature was dictated by the volatility of Li$_2$O, however, no appreciable Li losses were observed in our specimens. Neutron and x-ray powder diffraction revealed that there were 2–3% of extrinsic phases in the samples. The sample used in the neutron experiment was obtained from a different batch than the one used in the other measurements. This sample was prepared using isotopically pure $^7$Li$_2$CO$_3$.

The neutron powder-diffraction experiments were carried out on the high-resolution time-of-flight diffractometer HRPD at the ISIS spallation neutron source of the Rutherford Appleton Laboratory, UK. Data were recorded in the backscattering geometry (2$\theta_{ave}$ = 168°) over a time frame of 100 ms corresponding to a $d$-spacing window between 0.6 and 2.6 Å, spanned with an almost constant instrumental resolution $\Delta d/d$ of about 5 $\times$ 10$^{-4}$. Data were collected at several temperatures on warming from 2 to 300 K. Data
analysis of the diffraction patterns was performed using a Rietveld-method\textsuperscript{11} refinement program.\textsuperscript{12} Structural parameters, isotropic temperature factors (ITF), site occupation factors (SOF), and cell parameters were determined from single and automatic sequential refinements (typical $\chi^2 = 0.04$). The scattering lengths used in the refinement were $a_{La} = 8.24$ fm, $b_{Ni} = 10.3$ fm, $b_L = -2.22$ fm, and $b_O = 5.805$ fm. The x-ray powder-diffraction patterns were taken with a high-resolution Rigaku Goniometer (Bragg-Brentano geometry) using Cu $K\alpha$ radiation. The $T$-dependent measurements were performed between 15 and 300 K on cooling using a cryostat Cryomini Coldhead and a Rigaku PTC-20A $T$ controller with a precision of $\sim 0.2$ K. The data were analyzed by means of the Rietveld method using the DBWS9807 program.\textsuperscript{13} The observed Bragg peaks were indexed in the $Ammm$ space group (no. 65) for both neutrons and x-ray experiments. Nevertheless, the structure is metrically tetragonal, and the $a$ and $b$ lattice parameters were constrained as equal in all the refinements. Since the samples used in the neutron and x-ray experiments were from different batches and our interest was just to measure the $T$ dependence of $c/a$, we did not compare the calibration between the x-ray and neutron instruments.

The EPR experiments were carried out in Bruker $S$, $X$, and $Q$-band spectrometers, using a helium gas flux (4–300 K) $T$ controller. For these low-frequency measurements the magnetic field was calibrated with an NMR Gaussmeter. The high-frequency, 100–200 GHz, $W$-band EPR experiments were carried out in the National High Magnetic Field Laboratory at Tallahassee. The superconducting magnet at NHMF was calibrated with a DPPH marker sample. In all cases the magnetic-field homogeneity was better than $0.03$ G/cm$^3$. The susceptibility measurements were made in a Quantum Design dc superconducting quantum interference device (SQUID) magnetometer.

For the Raman scattering experiments, a JY T-64000 spectrometer equipped with a charge-coupled device (CCD) detector and a cold finger closed cycle He refrigerator were used. The sample was excited with the 5208-Å line of a Krypton laser focused in a diameter of $\sim 50$ $\mu$m. The incident power was kept below 10 mW.

III. EXPERIMENTAL RESULTS

Figure 1(a) presents the La$_2$Ni$_{0.5}$Li$_{0.5}$O$_4$ superstructure generated by the ordered occupation of Ni and Li atoms in two different sites, thus inducing the larger tetragonal unit cell ($a' = a/\sqrt{2}, c' = c$).\textsuperscript{10} Figure 1(b) shows the observed/calciumt neutron-diffraction patterns at 300 K, and their difference as an example. Neutron and x-ray profiles indicate only a partial Ni and Li ordering over the two metal sites ($2d$ and $2b$ of the $Ammm$ space group). The neutron diffraction is particularly sensitive to the ordering, due to the large difference between the scattering lengths of Ni and Li, besides being opposite in sign. The results obtained at 2 and 300 K are shown in Table I, and confirm previous x-ray structural determinations.\textsuperscript{10} Our x-ray powder profiles also show the presence of superlattice peaks associated to cation ordering. According to both experiments, the Li/Ni occupancies in the Ni(Li) site, refined in a partial disorder model, is $\sim 30\%$ (see Table I).

![La$_2$Ni$_{0.5}$Li$_{0.5}$O$_4$](image)

FIG. 1. (a) Unit cell of the superstructure induced by cation ordering in La$_2$Ni$_{0.5}$Li$_{0.5}$O$_4$ (space group Ammm, no. 65). Lighter and darker shaded octaedra are occupied by Ni and Li, respectively. La atoms are represented by spheres; oxygen atoms are not shown; (b) observed (full line), calculated (symbols), and difference (bottom) neutron-diffraction patterns for La$_2$Ni$_{0.5}$Li$_{0.5}$O$_4$ at 300 K. The sample used contained small amounts of La$_2$O$_3$ and NiO phases, which have been included in a multiphase Rietveld refinement. Traces of an unidentified, ill-crystallized phase are also present, as revealed by the broader peaks not reproduced by the calculated profile.

The $T$ dependence of the $c/a$ ratio, obtained from the refinement of neutron-diffraction patterns, is shown in Fig. 2. A small, but significant, increment of this ratio upon cooling is clearly observed. For comparison, the inset of Fig. 2 shows the $T$ dependence of $c/a$ obtained according to a Rietveld refinement of the x-ray patterns for the sample used in the EPR experiment. Although the neutron and x-ray experiments were done in samples coming from different batches, both techniques measured approximately the same change of $c/a$ ($\sim 0.025\%$) between high and low $T$.

Raman scattering is a useful tool for probing symmetry reduction, due to the associated increase of the Raman-allowed modes. The K$_2$NiF$_4$-type tetragonal structure allows for four Raman active modes ($3A_{1g} + B_{1g}$),\textsuperscript{6} while the Ammm cation-ordered structure presents 36 Raman modes ($12A_g + 10B_{1g} + 12B_{2g} + 2B_{3g}$).\textsuperscript{14} The unpolarized Raman spectrum of La$_2$Ni$_{0.5}$Li$_{0.5}$O$_4$ at $T = 10$ K is shown in Fig. 3. Within our experimental resolution, 14 modes were observed, at 103, 130, 164, 188, 233, 246, 272, 331, 348, 380, 424, 530, 694, and 752 cm$^{-1}$. These are more than the number of allowed modes for the tetragonal K$_2$NiF$_4$-type struc-
TABLE I. Structural parameters for La$_2$Ni$_{0.5}$Li$_{0.5}$O$_4$, refined from neutron powder profiles. Weighted profile $R$ factors $R=0.048$, $\chi^2=4.0$. Lattice parameters are given in angstroms.

<table>
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<tr>
<th>$T=2$ K</th>
<th>$T=300$ K</th>
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<tbody>
<tr>
<td>$a=5.29920(1)$</td>
<td>$a=5.31215(1)$</td>
</tr>
<tr>
<td>$b=5.29920(1)$</td>
<td>$b=5.31215(1)$</td>
</tr>
<tr>
<td>$c=12.85946(3)$</td>
<td>$c=12.88783(3)$</td>
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</tr>
<tr>
<td>$z$</td>
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<td>$\text{ITF}$</td>
<td>0.20(3)</td>
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<tr>
<td><strong>At</strong></td>
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<td>$\text{SOF}$</td>
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Figure 2. $T$ dependence of the $c/a$ lattice parameters ratio for La$_2$Ni$_{0.5}$Li$_{0.5}$O$_4$ measured by and prepared for neutron-diffraction experiments. The inset shows the $c/a$ ratio measured by and prepared for x-ray experiments. The full lines are a guide for the eye.

Figure 3. Unpolarized Raman spectrum, at $T=10$ K, for La$_2$Ni$_{0.5}$Li$_{0.5}$O$_4$. The observed mode frequencies are indicated.
La$_2$Ni$_{0.5}$Li$_{0.5}$O$_4$ is a paramagnetic system of spins $S=1/2$ ($g=2$, and $\mu_{\text{eff}}=1.73\mu_B$), in agreement with the above EPR results where the Ni$^{3+}$ ($3d^7$) ions are found in the $^2A_{1g}$ low-spin configuration state. Since the $g_{av}=(g_||+2g_\perp)/3$ is $T$ independent (see Fig. 5), we believe that the reduction in $\mu_{\text{eff}}$ below 50 K (see inset in Fig. 6) is probably associated to antiferromagnetic (AFM) correlations between the Ni$^{3+}$ ions due to the Ni(Li) occupancy disorder ($\sim 30\%$) found in these samples.

The distortion and broadening of the EPR resonances [Figs 4(a) and 6], and the decrease of $\mu_{\text{eff}}$ (inset of Fig. 6) observed at low $T$ indicates that short-range magnetic correlations may be present in our samples. The Ni(Li) occupancy disorder, observed in our neutron-diffraction experiments, may favor AFM correlation between the Ni$^{3+}$ ions. However, despite this low-$T$ magnetic interaction, the $g$-value anisotropy is clearly observed in our EPR experiments [see Figs. 4(a) and 5].

**IV. ANALYSIS AND DISCUSSION**

Disorder of Li and Ni atoms on the 2$b$ and 2$d$ positions of the Ammm space group was allowed in the Rietveld refinement of our neutron-diffraction data. Equal isotropic temperature factors have been used to avoid correlation with the Li/Ni site occupation factors (SOF). The results obtained show partial ordering of Ni and Li over the two metal sites, with Ni atoms being preferentially located on the $2b$ positions (SOF $\approx 0.7$, see Table I). Warda et al. proposed a “twin” model to justify the apparent absence of a complete ordered distribution of the cations on the octahedral sites of the La$_2$Ni$_{0.5}$Li$_{0.5}$O$_4$ crystal structure. According to this model, domains of an ordered structure are present in two orientations, the twin plane being (110). Our powder neutron-diffraction results are consistent with a partially ordered structure. But, the presence of small amounts of secondary phases in the sample used prevented a careful analysis of the diffuse scattering contribution to the diffraction patterns, so that we are not able neither to confirm nor to dismiss the model described in Ref. 10. However, the sharp peaks of the Raman spectra (see Fig. 3) indicate that, at least in part of our sample, there is long-range ordering.

The EPR data of Figs. 4 and 5 and the magnetization measurements (inset in Fig. 6) show that in La$_2$Ni$_{0.3}$Li$_{0.7}$O$_4$ the nickel ions are in the Ni$^{3+}$ ($3d^7$) oxidation state with the $^2A_{1g}$ low-spin configuration, $S=1/2$ as a ground state. The nickel ions are in the Ni$^{3+}$ ($3d^7$) oxidation state with the $^2A_{1g}$ low-spin configuration, $S=1/2$ as a ground state. At room temperature the c/a ratio for La$_2$Ni$_{0.5}$Li$_{0.5}$O$_4$ ($\approx 2.43$, see Fig. 2) is larger than that in La$_2$Ni$_{0.5}$O$_{4+\delta}$ ($\approx 2.32$). This is due to a considerable tetragonal elongation of the NiO$_6$ octahedra induced by the Li$^+$ doping and hole localization at this site. This would favor the Ni$^{3+}$ ($3d^7$)
oxidation state with the $^2A_{1g}$ low-spin configuration as a ground state. A relatively large splitting of the $^2E_g$ ($^6T_{2g}$,$^4T_{2g}$) state, $^2B_{1g}$-$^2A_{1g}$ = 4 $\delta_1$, can be anticipated for this system.\textsuperscript{15} Now, the increasing $c/a$ values at low $T$ (see Fig. 2) indicates that the NiO$_6$ octahedra become more elongated, stabilizing even more the Ni$^{3+}$ $^2A_{1g}$ low-spin configuration. We will show that this is consistent with the $T$ dependence of the $g$ values measured in our EPR experiments (see Figs. 4 and 5).

In the following we will describe a calculation that will be consistent with the $T$ dependence of the $g$ value shown in Fig. 5.\textsuperscript{16} A tetragonal distortion, of Jahn-Teller origin or caused by the presence of Li$^+$ in the neighboring sites, splits the cubic levels $^2E_g$ into $^2A_{1g}$ and $^2B_{1g}$ (separated by 4 $\delta_1$) and $^4T_{2g}$ into $^4A_{2g}$ and $^4E_g$ (separated by 3 $\delta_2$). The neutron and x-ray results for the $c/a$ measurements indicate that there is an elongation of the oxygen octahedra in the $z$ direction (see Fig. 2). This, and the EPR results, suggests $^2A_{1g}$ as a ground-state with the excited states $^4A_{2g}$, $^4E_g$, and $^2B_{1g}$ at $\delta_{2,4}$, $\delta_{2,4} + 3 \delta_2$, and 4 $\delta_1$, respectively.\textsuperscript{15} We diagonalize the spin-orbit interaction, $H_{SO} = \sum \zeta_{i} \hat{s}_{i} \cdot \hat{l}_{i}$, within that manifold. The $^2B_{1g}$ state is not included in the calculation because 4 $\delta_1 \gg 3 \delta_2$.\textsuperscript{15} The values of $g_1$ and $g_2$ for the ground state are obtained from this diagonalization. Both $g$ values are a function of $\delta_{2,4}$ and $\delta_2$. That dependence is shown in Fig. 7 for 0.0 $\leq \delta_{2,4}/\zeta \leq 4.0$ (using $\zeta = 500$ cm$^{-1}$) for nine different values of $\delta_2$ (800 $\leq \delta_2 \leq 2400$ cm$^{-1}$). Analyzing the various simulations in Fig. 7 we notice that a change of $\delta_{2,4}/\zeta (<5\%)$ around the value that yields to the observed $g$ values ($\delta_{2,4}/\zeta = 2.4$), introduce changes in $g_2$ in the experimental error, thus, $g_1$ is primarily determined by $\delta_2$. We use this fact to find the $\delta_2$ values at 5 and 271 K that best adjust the measured $g_{||}$ values. These values are: $\delta_2(5 \text{K}) = 2360$ cm$^{-1}$ and $\delta_2(271 \text{K}) = 1020$ cm$^{-1}$. Now, using these values for $\delta_2$ we find the ratios $\delta_{2,4}/\zeta$, at low and high $T$, that give the best agreement with the observed values for $g_{\perp}$. These values are: $\delta_{2,4}(5 \text{K})/\zeta = 2.41$ and $\delta_{2,4}(271 \text{K})/\zeta = 2.33$. The $g$ values obtained theoretically by this procedure are: $g_{||}(271 \text{K}) = 2.0153$; $g_{||}(5 \text{K}) = 2.0055$ and $g_{\perp}(271 \text{K}) = 2.2529$; $g_{\perp}(5 \text{K}) = 2.2608$. These values are in very good agreement with the measured values in $W$ band: $g_{||}(271 \text{K}) = 2.015(1)$; $g_{||}(5 \text{K}) = 2.006(2)$, and $g_{\perp}(271 \text{K}) = 2.253(1)$; $g_{\perp}(5 \text{K}) = 2.261(2)$. To the best of our knowledge there is no available simple microscopic theory connecting a change in $c/a (T)$ with a change in the tetragonal crystal-field parameters that can be used to fit the $T$ dependence of the $g$ values with $c/a (T)$. We should mention that the energy levels for Ni$^{3+}$ in an octahedral field subjected to a tetragonal elongation were calculated previously\textsuperscript{17} and it is consistent with our results, i.e., it was found that $\delta_{2,4}$ should be almost independent of the elongation, while $3 \delta_2$ should increase substantially, and $\delta_{2,4} \approx 3 \delta_2$. From the values obtained for $\delta_{2,4}$ and $\delta_2$ (at $T = 5 \text{K}$ and $T = 271 \text{K}$) and taking the cubic splitting between $^4T_{1g}$ and $^2E_g$ the value\textsuperscript{10} of 1.35 $\times 10^3$ cm$^{-1}$, we obtained the level schemes given in the inset of Fig. 7.

From the above calculated $g$ values, we found that the larger $g$-value anisotropy, $g_{\perp} - g_{||}$, measured at low $T$ leads to a larger crystal-field levels separation (see inset in Fig. 7). Therefore we conclude that the increase of $c/a$, measured at low $T$ in this work for a polycrystalline sample of La$_2$Ni$_{0.5}$Li$_{0.5}$O$_4$, can be interpreted in terms of the stabilization of the $^2A_{1g}$ low-spin configuration in the NiO$_6$ Jahn-Teller distorted octahedra.

V. CONCLUSIONS

In summary, structural and magnetic properties of La$_2$Ni$_{0.5}$Li$_{0.5}$O$_4$ were investigated. The observed intensity of the neutron and x-ray superlattice Bragg peaks are consistent.
with a partial ordering of the Ni and Li cations and/or a ‘‘twin’’ domain structure. However, our Raman-scattering experiments support a long-range ordering, at least in part of our sample. EPR experiments showed a $g$-value anisotropy that increases at low $T$. That was interpreted in terms of a further stabilization of the Ni $^{3+}$ $^{2}A_{1g}$ low-spin configuration. This was supported by the increase of the $c/a$ lattice parameters ratio measured at low $T$ and the $g$-values calculations. Our magnetization measurements also confirmed that La$_2$Ni$_{0.5}$Li$_{0.5}$O$_4$ is a paramagnetic system of spins $S=1/2$ ($g=2$, and $\mu_{\text{eff}}=1.73\mu_B$), in agreement with the EPR results reported in this work.

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