PHYSICAL REVIEW B VOLUME 30, NUMBER 11 1 DECEMBER 1984

Magnetic order or charge-density wave in La_2NiO_4 by Mössbauer spectroscopy

J. Fontcuberta
Facultat de Física, Universitat de Barcelona, Diagonal 645, Barcelona 28, Catalunya, Spain

G. Longworth
Nuclear Physics Division, Atomic Energy Research Establishment (Harwell), Oxforshire OX11 0RA, England

J. B. Goodenough
Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, England

(Received 17 February 1984; revised manuscript received 31 May 1984)

Measurements of Mössbauer absorption spectra of $^{57}Fe:La_2NiO_4$ at 297, 77, and 4.2 K provide evidence, at the lowest temperatures, of magnetic order in a sample containing $^{57}Fe^{3+}$-ion impurities and some $La_{2+n}Ni_{1+n}O_{4+3n}$ intergrowth. Mössbauer emission spectra of $^{57}Co:La_2NiO_4$ at 77 and 4.2 K show magnetic order coexisting with paramagnetism in a sample containing a small concentration of ^{57}Co-ion impurities and some $La_{2+n}Ni_{1+n}O_{4+3n}$ intergrowth. These results are interpreted as evidence for competition between magnetic ordering and charge-density-wave formation among electrons of a narrow $\sigma^*_{x^2-y^2}$ band; intergrowths, impurities, and nonstoichiometry favor magnetic ordering.

I. INTRODUCTION

Transition-metal compounds with the tetragonal K_2NiF_4 structure have been extensively studied because antiferromagnetic interatomic interactions between transition-metal ions in this structure are nearly two-dimensional. Whereas the $3d$ electrons in transition-metal halides are invariably localized, they may be either itinerant or localized in transition-metal oxides.[1] It is therefore of particular interest to explore this phenomenon in two-dimensional systems where anisotropic bonding may result in itinerant electrons in basal-plane d orbitals, but localized (strongly correlated) electrons in d orbitals oriented parallel to the unique axis.[2]

Recent structural refinement[1] of La_2NiO_4 has confirmed the K_2NiF_4 structure over a temperature range from 77 to 773 K. The unit cell ($c/a > 1$) increases continuously with temperature. By comparison with the magnetic properties of NiO ($T_N = 520$ K and Ni—O—Ni distance 3.86 Å), it has been suggested[1] that in La_2NiO_4 the Ni^{2+} $d_{x^2-y^2}$ orbitals σ bonding in the basal plane form a narrow $\sigma^*_{x^2-y^2}$ band of strongly correlated, itinerant-electron orbitals of $d_{x^2-y^2}$ parentage. The σ-bonding Ni^{2+} d_{z^2} orbitals have a much smaller d_{z^2}-O:p_σ-d_{z^2} overlap integral in the basal plane and only Ni-O-La-O-Ni interactions along the c axis; therefore the d_{z^2} orbitals would be localized in this structure.

Electrical-conductivity measurements show a smooth semiconductor-metal transition in the temperature range from 500 to 620 K, depending on the stoichiometry.[3] The magnetic susceptibility above 200 K exhibits a Curie-Weiss law with $\mu_{\rm eff} \approx 3.03\mu_B$ (only a little larger than the spin-only value expected for a localized-electron $S = 1$ configuration per molecule) and a large, negative Weiss constant $\Theta = -500$ K indicative of strong antiferromagnetic coupling within the basal planes.[2] Below 200 K there is an anomalous increase in the susceptibility relative to the values extrapolated from the high-temperature Curie-Weiss law. At lowest temperatures ($T \leq 50$ K) the measured $\mu_{\rm eff} \approx 1.83\mu_B$ is close to the value expected for one localized electron ($S = \frac{1}{2}$) per molecule, and the Weiss constant is $\Theta = -120$ K.[2]

At $T > 200$ K localized d_{z^2} spins appear to induce, via intra-atomic exchange, a localized parallel-spin density from the $\sigma^*_{x^2-y^2}$ band electrons; a strong correlation among the electrons of the half-filled $\sigma_{x^2-y^2}$ band would give rise to the observed $\mu_{\rm eff} \approx 3.03$ μ_B.

In the absence of any evidence from neutron-diffraction data for long-range antiferromagnetic order, it has been suggested[2] that the inflection in the resistivity and in the inverse magnetic-susceptibility—versus—temperature curves at 200 K may be due to a splitting in two of the narrow, half-filled $\sigma^*_{x^2-y^2}$ band as a result of cooperative displacements of the O^{2-} ions in the Ni—O—Ni basal planes. Such a splitting would reduce, if not eliminate, the indirect-exchange coupling of the localized d_{z^2} electron spins via the itinerant electrons of a half-filled $\sigma^*_{x^2-y^2}$ band.

Such displacements would represent a two-dimensional charge-density wave (CDW) with a charge disproportionation on $Ni^{(2\pm\delta)}$ ions. Stabilization of a CDW can open up an energy gap that splits occupied states from empty $\sigma^*_{x^2-y^2}$-band states. Alternatively, long-range two-dimensional magnetic order would split a narrow $\sigma^*_{x^2-y^2}$ band in two, but such an ordering is expected to give a different low-temperature behavior of the magnetic susceptibility and to be directly verifiable by neutron diffraction.[4]

To get more insight into the lack of any apparent long-range antiferromagnetic order at low temperature, it is interesting to use a microscopic tool like Mössbauer spectroscopy. Mössbauer spectroscopy is particularly useful for investigations of time-dependent physical processes having characteristic times $\tau \gtrsim 10^{-7}$ s. Magnetic relaxation, for example, can be easily monitored by Mössbauer spectroscopy. A $\tau > 10^{-7}$ s is found below a long-range magnetic ordering temperature T_C or T_N, and this condition evolves through $\tau \sim 10^{-7}$s with increasing temperature above T_C or T_N. In the presence of small magnetic clusters, the condition $\tau > 10^{-7}$ s is only accomplished at a temperature below T_C or T_N for the cluster.

To monitor magnetic relaxations, the ^{57}Fe Mössbauer nucleus can be used as an absorber of a 14.4-keV γ radiation from a suitable ^{57}Co-containing source (absorption spectroscopy); or if ^{57}Co is introduced into the material under study, the resonance can be obtained by using a ^{57}Fe containing standard absorber (emission spectroscopy). In both cases, the 14.4-keV radiation emitted by an excited ^{57}Fe nucleus is used to obtain information about the surrounding of that decaying nucleus.

This paper reports the Mössbauer absorption of ^{57}Fe-doped La_2NiO_4 and the Mössbauer emission spectroscopy of ^{57}Co-doped La_2NiO_4. The aim of this work was to search for any magnetic order as well as to look for a possible disproportionation of the isomer shift of the ^{57}Fe impurities.

In the first step of this work, results were obtained for the absorber case ($^{57}Fe{:}La_2NiO_4$). In order to obtain a reasonable absorption rate, it is necessary to dope the La_2NiO_4 oxide with a large amount of ^{57}Fe (0.26 wt %).

Such a high level of doping could significantly modify the physical properties of the particular material under the study. In order to avoid this problem, it seemed worthwhile to study in addition the Mössbauer emission spectroscopy of $^{57}Co{:}La_2NiO_4$, which requires a much smaller doping level (a few ppm).

II. EXPERIMENTAL

The ^{57}Fe-doped La_2NiO_4 was prepared by dissolving stoichiometric quantities of high-purity La_2O_3 (99.9%) and NiO (99.9%) in dilute HNO_3. La_2O_3 was previously heated overnight at 1000 °C in air to remove moisture and CO_2. The isotope ^{57}Fe in a metallic form was added to the solution in a concentration of 0.26% of the total weight of La_2NiO_4.

The solution was heated to dryness (150 °C). The resulting material was ground and heated in air for 4 h at 500 °C. The sample was reground, pelletized, and heated for 24 h at 1150 °C in air with periodic removal for regrinding and repelletizing.

The La_2NiO_4 necessary to prepare the source was synthesized by mixing the appropriate amounts of the corresponding oxides followed by systematic grinding and firing at 1200 °C in air atmosphere. A pellet of this latter product was made active by dropping onto its surface a $^{57}CoCl_2$ solution and then heating until dry. Diffusion of the ^{57}Co into the sample was carried out at 1150 °C for 48 h. The sample was cooled down slowly in the furnace. Any surface activity was removed by cleaning the pellet with dilute HCl. The final activity of the sample was about 4 mCi. A nonactive sample was synthesized together with the active one in order to check the structure of the final compound.

X-ray powder patterns at room temperature were recorded on a conventional Philips diffractometer using Cu $K\alpha$ radiation. Cell constants were refined with a least-squares program (AFFMA) on the basis of the tetragonal K_2NiF_4 structure ($I/4mmm$) by using 36 and 39 reflections ($K\alpha_1$, $K\alpha_2$) for the ^{57}Fe-doped La_2NiO_4 and for the inactive samples, respectively.

The lattice parameters obtained from the fitting ($^{57}Fe{:}La_2NiO_4$, $a = 3.868 \pm 0.001$ Å and $c = 12.663 \pm 0.005$ Å; La_2NiO_4, $a = 3.867 \pm 0.001$ Å and $c = 12.665 \pm 0.006$ Å) are in good agreement with those reported in Refs. 1 and 2. No unindexable lines on the $I/4mmm$ symmetry group were observed.

The Mössbauer spectra were obtained at 298, 77, and

TABLE I. Parameters obtained from Mössbauer absorption spectra measured at temperatures of 297, 77, and 4.2 K with a $^{57}CoRh$ source. IS is the isomer shift relative to metallic iron. QS is the quadrupole splitting. HF and DHF are the hyperfine magnetic field and its standard deviation, respectively; % is the percentage of the total area, and χ^2 is a measure of quality of the fit. Γ is the observed linewidth.

T (K)	IS (mm/s)	QS (mm/s)	HF (kOe)	DHF (kOe)	Γ (mm/s)	%	χ^2
297	0.322(1)	1.440(4)			0.29(3)	68(2)	
	0.295(5)	0.85(2)			0.31(2)	19(4)	1.13
	0.267(6)	0.40(3)			0.29(2)	13(4)	
77	0.50(8)				5.7(5)	30(6)	
	0.448(2)	1.49(5)			0.38(3)	53(2)	1.02
	0.465(2)	0.82(3)			0.25(2)	6(3)	
	0.448(2)	0.46(3)			0.34(3)	11(3)	
4.2	0.454(2)	−0.30(9)	472	13	0.20(0)	41(6)	
	0.47(1)	−0.31(1)	447	13	0.20(0)	25(10)	1.06
	0.45(5)	−0.22(3)	422	30	0.20(0)	34(6)	

TABLE II. Parameters obtained from Mössbauer emission spectra measured at 297, 77, and 4.2 K with a PdFe absorber. The symbols IS, QS, HF, DHF, and χ^2 have the same meaning as in Table I.

T (K)	IS (mm/s)	QS (mm/s)	HF (kOe)	DHF (kOe)	Γ (mm/s)	%	χ^2
297	0.23(1)	1.30(2)			0.50(6)	38(8)	1.19
	0.25(2)	0.86(4)			0.29(7)	17(10)	
	0.23(1)	0.44(1)			0.41(2)	45(7)	
77	0.47(3)	1.28(4)			1.1(2)	35(3)	1.03
	0.35(1)	0.69(2)			0.64(2)	39(10)	
	0.23(16)	−0.2(1)	395	51	0.20	20(6)	
	0.15(22)	0	170	26	0.20	6(4)	
4.2	0.32(8)	1.9(5)			1.6(5)	11(7)	1.09
	0.34(3)	−0.19(2)	467	49	0.20	24(4)	
	0.34(4)	−0.12(2)	435	38	0.20	65(2)	

4.2 K with a constant-acceleration spectrometer. The data were stored in a 1024-channel analyzer. A ^{57}CoRh source was used in the absorber experiments. In the emission experiments a PdFe absorber (0.1749 mm/s versus α-Fe) was carried by the drive unit. In both cases calibration was done via a metallic-iron absorber and a ^{57}CoRh source. The fitting procedure was as follows.

(i) In the paramagnetic phase, Lorentzian lines and Voigt lines were used. The latter were adopted because of the better quality of the fit (smaller χ^2 values).

(ii) In the magnetically ordered phase, the fitting was carried out with two different methods: (a) Six Lorentzian lines were used for each hyperfine magnetic field (HF) with the usual 3:2:1:1:2:3 intensity ratio. (b) A Gaussian distribution of hyperfine fields was used for each HF. The standard deviation of this distribution is denoted by DHF. In that case, the natural linewidth was assumed for each component.

The latter method (b) was adopted due to the lowest χ^2 values reached in all cases. All the relevant Mössbauer parameters are summarized in Tables I and II according to the above discussion.

III. RESULTS AND DISCUSSION

A. ^{57}Fe:La$_2$NiO$_4$

The Mössbauer spectra recorded at three different temperatures are plotted in Figs. 1(a), 2(a), and 3(a). The relevant parameters obtained from the fitting are in Table I. The room-temperature spectrum [Fig. 1(a)] shows two broad fingers, and it has been fitted with a superposition of three quadrupole doublets; their different isomer shifts (IS) and quadrupole splittings (QS) reflect the existence of three distinct environments and/or electronic states for the iron impurities in the lattice. Due to the poor resolution of the smallest doublets, the relative calculated intensities are not very reliable.

In the ideal K$_2$NiF$_4$ structure of La$_2$NiO$_4$, all the Ni^{2+} positions are equivalent. If we assume that all the ^{57}Fe impurities go into nickel positions, we should observe only one quadrupole doublet according to the tetragonal ($c > a$) symmetry of the coordination polyhedron. The reported Mössbauer results on isostructural LaSrFeO$_4$, for example, show the presence of a single quadrupole doublet (QS value of 1.4 mm/s, IS value of 0.33 mm/s) at room temperature,[5] characteristic of an Fe^{3+} ion in a high-spin state in a distorted-octahedral coordination. Consequently we can assign the doublet of highest intensity and largest quadrupole splitting to Fe^{3+} ions occupying Ni^{2+} regular positions in the structure.

The room-temperature Mössbauer spectrum obtained for ^{57}Fe:La$_2$Li$_{1/2}$Co$_{1/2}$O$_4$ (Ref. 6) consists of three quadrupole doublets with IS values of 0.37, 0.25, and −0.19 mm/s and QS values of 0.61, 1.84, and 1.08 mm/s, respectively; these three different spectra could be attributed to high-spin and intermediate-spin states of Fe^{3+} and to Fe^{4+}, respectively. This observation suggests that

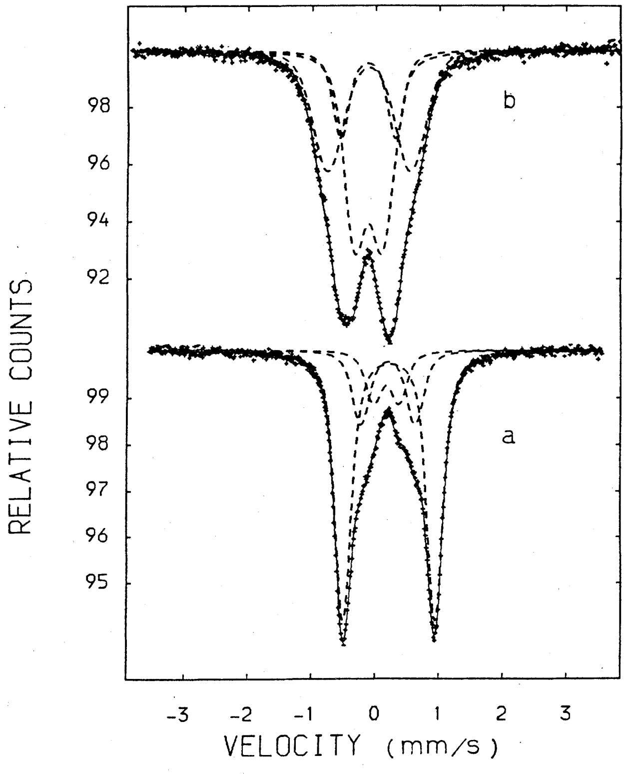

FIG. 1. Mössbauer spectra of (a) ^{57}Fe:La$_2$NiO$_4$, and (b) ^{57}Co:La$_2$NiO$_4$ at 297 K.

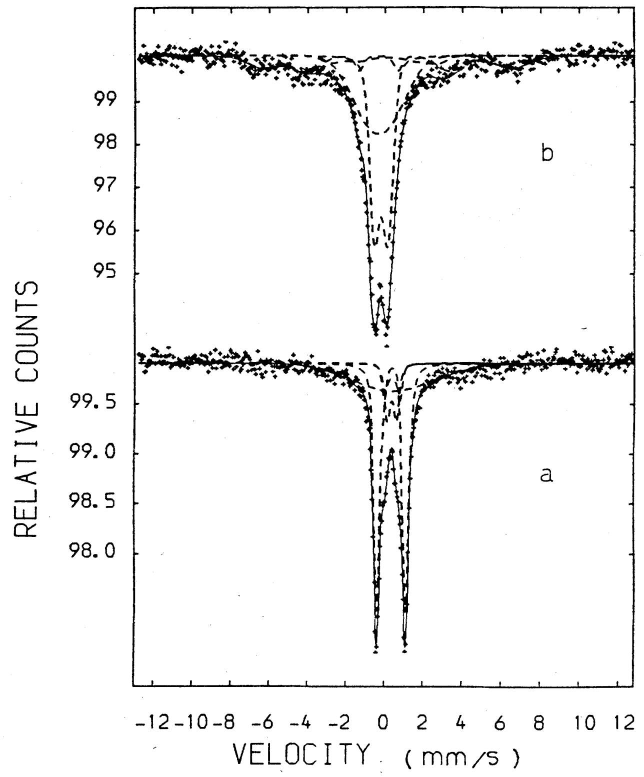

FIG. 2. Mössbauer spectra of (a) ^{57}Fe:La$_2$NiO$_4$, and (b) ^{57}Co:La$_2$NiO$_4$, at 77 K.

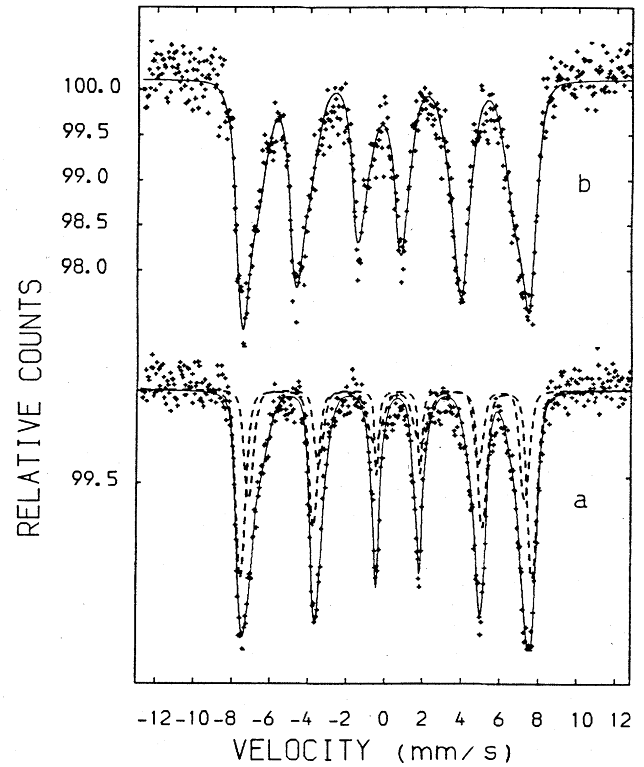

FIG. 3. Mössbauer spectra of (a) ^{57}Fe:La$_2$NiO$_4$, and (b) ^{57}Co:La$_2$NiO$_4$ at 4.2 K.

the quadrupole doublets with IS values of 0.295 and 0.267 mm/s might be tentatively assigned to iron atoms in a intermediate electronic configuration such as $(d_{yz}d_{xz})^3 d_{xy}^1 d_{z^2}^1 d_{x^2-y^2}^0$, or $(d_{zy}d_{xz})^4 d_{xy}^1$.

However, a more plausible explanation can be given on the basis of Fe^{3+} ions in different structural positions. It is well known[7] that, unless great care is taken in preparation, nominal La$_2$NiO$_4$ generally contains some intergrowth phases, La$_{2+n}$Ni$_{1+n}$O$_{4+3n}$. These intergrowths can trap holes observed by iodometric titration,[1] and they can be seen directly in the electron microscope.[7] It is therefore expected that different atomic surroundings may be available for the substitutional Fe^{3+} impurity, especially since the higher formal valence on Fe^{3+} (versus Ni^{2+}) would favor stabilization of the intergrowths.

The intergrowth phase is built by incorporation of additional LaNiO$_3$ perovskite layers between the La-O layers. The initial c-axis sequence is

La—O—Ni—O—La ,

and an additional perovskite layer gives two contiguous Ni ions:

La—O—Ni—O—Ni—O—La .

With three contiguous

La—O—Ni—O—Ni—O—Ni—O—La

or more, the center Ni are in a perovskite slab and have two c-axis Ni-atoms near neighbors for any thickness of the perovskite slab.

Since the number of c-axis near-neighbor Ni atoms increases, the mean c-axis Ni—O distance decreases, so the quadrupole splitting and isomer shift should decrease; moreover, three distinguishable spectra should be observed. This is in agreement with our results.

In summary, we interpret the two smallest quadrupole splittings with IS values of 0.29 and 0.27 mm/s as due to the Fe^{3+} ions occupying octahedrally coordinates sites with one and two near-neighbor Ni atoms along the c axis as a result of one or two neighboring perovskite intergrowth layers.

The apparently important volume of the intergrowths ($\sim$39%) observed by Mössbauer spectroscopy, which is a local probe, is not contradictory with the failure to observe intergrowths with x-ray diffraction. Independent estimation of the relative concentration of intergrowths can only be obtained with electron microscopy.[7] Moreover, Fe^{3+} can be expected to substitute preferentially for Ni^{3+} in the perovskite blocks.

At 77 K, the Mössbauer spectrum [Fig. 2(a)] shows three quadrupole splittings—see Table I—with QS values essentially the same as those at room temperature. Such a situation is generally found for Fe^{3+} high-spin compounds in which only the lattice contribution to the electric field gradient (EFG) appears in the quadrupole splitting. This observation seems to rule out the assignment of the low IS values to some intermediate electronic configuration; it is consistent with the intergrowth model.

The IS values of about 0.45 mm/s show the usual increase with respect to the room-temperature values due to the second-order Doppler effect. From the theoretical slope $d(\mathrm{IS})/dT=7.3\times10^{-4}$ mm/s K obtained for a solid below its Debye temperature, an increase of about 0.16 mm/s is expected. This is in good agreement with our observed increases (0.13—0.18 mm/s) over the room-temperature values. It is important to realize that at 77 K a broad resonance line appears in the spectrum together with a broadening of some of the absorption lines [see Table I and Fig. 2(a)].

At 4.2 K [Fig. 3(a)] all the quadrupole doublets split into sextets as a result of the nuclear Zeeman effect. A hyperfine magnetic field at the $^{57}\mathrm{Fe}^{3+}$ nucleus shows the existence of either long-range magnetic order or a short-range ordering with a slow magnetic relaxation. No magnetic order, not even short-range order, had been observed by susceptibility and neutron-diffraction techniques. The Mössbauer effect shows that the characteristic relaxation time of the internal magnetic field is longer than 10^{-7} s.

If a hyperfine magnetic field coexists with a quadrupole interaction in a nucleus, the quadrupole shift of each hyperfine component is given by

$$(\mathrm{QS})_1=eqQ(3\cos^2\theta-1)/8\ , \tag{1}$$

where Q is the nuclear quadrupole moment, q is the major (V_{ZZ}) component of the EFG, and θ is the angle between H_{hf} (the quantization axis) and V_{ZZ}. This expression holds for a perturbative treatment and an axial EFG.

The measured quadrupole splitting in the paramagnetic phase is given by

$$(\mathrm{QS})_2=eqQ/2\ . \tag{2}$$

Introducing the 4.2 K value of $(\mathrm{QS})_1\sim-0.3$ mm/s and the room-temperature value of $(\mathrm{QS})_2\sim1.44$ mm/s into Eqs. (1) and (2) gives $\theta\sim76°$.

If we assume that the magnetic hyperfine-field vector H_{hf} lies in the basal plane, as in $\mathrm{LaSrFeO_4}$,[5] it follows that the V_{ZZ} component of the EFG points in a direction that is far ($\theta\sim14°$) from the c axis.

In this deduction we have supposed that the quadrupole splitting at 4.2 K is the same (1.44 mm/s) as in the room-temperature case. However, if the onset of short-range magnetic order within the basal planes changes the Ni—O distances in the basal planes relative to those along the c axis, then the quadrupole splitting would change. Such a change would be a manifestation of magnetostriction and/or exchange restriction. A change of $eqQ/2$ from 1.4 to 1.2 mm/s would be sufficient to explain the experimental data, assuming that the V_{ZZ} remains in the [001] direction.

The fact that there is no evidence from the IS of a disproportionation into two crystallographically distinguishable regular positions for Ni^{2+} ions appear to rule out the presence of a charge-density wave below 200 K, at least in this sample. However, the Fe^{3+} ion does not participate in the disproportionation (CDW) and any change in IS due to small O^{2-}-ion displacements may not be resolvable. In addition, the presence of an ion that does not participate in the CDW would tend to suppress any nearest-neighbor O^{2-} displacements. The existence of a broad line at 77 K centered at about 0.50 mm/s can therefore be attributed to an incipient magnetic splitting. However, it is quite unrealistic to fit this central line with a six-line spectrum because relaxation effects may be present and the overlapping is large. The strong correlation between the Mössbauer parameters obtained by including a six-line spectrum makes the fitting unreliable. The appearance of a well-resolved six-line spectrum demonstrates the presence of some type of magnetic order at 4.2 K in this sample.

In principle care must be taken with this conclusion because only a short-wavelength, commensurable CDW would give rise to resolvable isomer shift. An incommensurate CDW would produce non-Lorentzian line shapes without distinguishable lattice sites for the Mössbauer ion. Moreover, the Voigt profile used in our curve fitting comes from the convolution of a Lorentzian line with a Gaussian distribution arising from *any* instrumental or physical disturbances. However, we found no evidence of an increase in the Gaussian component at low temperatures that could be attributed to the onset of an incommensurate or commensurate with long-wavelength CDW.

An incipient magnetic splitting at 77 K is suggestive of a long-range Néel temperature $T_N\lesssim77$ K. If the anomaly at 200 K in $\mathrm{La_2NiO_4}$ is due to the onset of short-range magnetic order, the atomic-moment direction within a magnetically ordered cluster must fluctuate with a relaxation time $\tau_R<10^{-7}$ s in the temperature interval $77<T<200$ K.

In summary, the Mössbauer data show no evidence for a CDW in the $\sigma^*_{x^2-y^2}$ band below $T_t\approx200$ K in our sample of 0.26 weight-percent Fe-doped $\mathrm{La_2NiO_4}$. Instead, it is consistent with a long-range magnetic order at 4.2 K having a $T_N\lesssim77$ K. In view of the evidence, from paramagnetic susceptibility data, for strong antiferromagnetic interactions among the $\sigma^*_{x^2-y^2}$ electrons at temperatures $T>T_t\approx200$ K in pure $\mathrm{La_2NiO_4}$, a long-range antiferromagnetic ordering would be expected if any CDW is suppressed by introduction of 0.26 wt. % iron. Suppression of the CDW would require $T_t<T_N$ and hence a rapid lowering of T_t with increasing dopant concentration. Since the Fe^{3+} ions would not participate in the CDW, their substitution must lower T_t; however, the extent of the effect is not obvious. To obtain more insight into a lower dopant concentration, this could only be done with Mössbauer emission spectroscopy.

B. $^{57}\mathrm{Co{:}La_2NiO_4}$

From the relative ionic sizes, we may assume that the $^{57}\mathrm{Co}$ impurity substitutes for Ni in $\mathrm{La_2NiO_4}$. The p-type character of pure $\mathrm{La_2NiO_4}$ places the Fermi energy near the top of the $\mathrm{Ni}^{3+/2+}{:}3d^8$ band.[2] Cobalt, being lighter than nickel, has its $\mathrm{Co}^{3+/2+}{:}3d^{87}$ couple above the $\mathrm{Ni}^{3+/2+}$ couple, so the cobalt substitutes as an acceptor center, it enters the lattice as $^{57}\mathrm{Co}^{3+}$ as long as the concentration of cobalt is less than the concentration of holes in the $\mathrm{Ni}^{3+/2+}{:}3d^8$ band of the host structure. In the absence of any anomalous behavior associated with electron capture by the nucleus,[8] $^{57}\mathrm{Fe}^{3+}$ is obtained from $^{57}\mathrm{Co}^{3+}$.

As could therefore be anticipated, the room-temperature source spectrum, Fig. 1(b), is similar to that found in the absorber case. It could be fitted with three different quadrupole doublets each having a slightly distinct isomer shift; see Table II. The close similarity between the quadrupole splittings obtained from Figs. 1(a) and 1(b) allows an assignment of the three room-temperature quadrupole doublets in $^{57}Co:La_2NiO_4$ similar to that for $^{57}Fe:La_2NiO_4$. The Fe daughter in regular positions has an QS value of 1.29 mm/s; those in the intergrowth phases, $La_{2+n}Ni_{1+n}O_{4+3n}$, have QS values of 0.86 and 0.44 mm/s.

The principal difference between the spectra of Figs. 1(a) and 1(b) is the relative intensities of the three quadrupole doublets. In fact, it is extremely difficult to obtain truly stoichiometric La_2NiO_4;[1] it is even more difficult to obtain products of equivalent stoichiometry in two different syntheses. However, the higher percentage of dopant in the intergrowth phases in $^{57}Co:La_2NiO_4$ versus $^{57}Fe:La_2NiO_4$ does not need to imply significant differences in intergrowth concentrations; the different site preferences of Fe^{3+} and Co^{3+} ions ensure different dopant distributions even with similar intergrowth concentrations.

In fact, however, we should anticipate a different intergrowth configuration in the $^{57}Co:La_2NiO_4$ sample because of our doping method. Diffusion of surplus cobalt from the surface will be met by a counter diffusion of La^{3+} ion to form perovskite layers. Once the perovskite intergrowth layers are formed, they are stable; but some diffusion of the cobalt into the bulk can proceed by Ni-Co interchange. Therefore, the percentage of $^{57}Co^{3+}$ in regular Ni^{2+} positions is expected to be smaller than the corresponding percentage of $^{57}Fe^{3+}$. From our data (Tables I and II) the concentrations of $^{57}Fe^{3+}$ in regular sites in the ^{57}Co-doped and ^{57}Fe-doped samples are 38% and 68%, respectively. From this observation, we may assume that there is a higher density of intergrowth near the surface in the $^{57}Co:La_2NiO_4$ sample, and that there is therefore a higher probability of forming a perovskite layer at the surface.

The isomer shifts in the emission spectrum are only a little smaller than those observed in the absorption spectrum, and we can assign them to high-spin Fe^{3+} ions. It may be argued that an IS of about 0.23 mm/s with respect to elemental Fe corresponds to intermediate-spin iron. However, the QS values would, in that case, be strongly temperature dependent. The close similarity of the QS values at 297 and 77 K seems to rule out any intermediate-spin hypothesis. The intensity of the internal magnetic field measured at 77 K (and 4.2 K) also supports a high-spin assignment.

The 77-K Mössbauer emission spectrum, Fig. 2(b), shows two fingers and a superimposed six-line spectrum. The total intensity of the magnetic compound is under 26% of the total intensity, but the hyperfine field of about 400 kOe is only about 12% smaller than its value at 4.2 K.

These data indicate that at 77 K, regions of magnetic order having a relaxation time $\tau_R > 10^{-7}$ s coexist with paramagnetic regions and/or with magnetically ordered clusters having a $\tau_R < 10^{-7}$ s. The large hyperfine field of the magnetically ordered phase—or cluster—indicates a magnetic ordering temperature $T_N \gg 77$ K within a magnetic cluster. The appearance of a six-line Mössbauer spectrum near 77 K would therefore seem to be associated with a $\tau_R > 10^{-7}$ s and a magnetic ordering temperature $T_N \gg 77$ K for an intergrowth-rich region. It is necessary to perform further experiments on the dependence of the HF and the relative fraction of the magnetically ordered phase as a function of temperature before any qualitative measure of the relaxation time can be given.

From Table II, about half of the intergrowth perovskite slabs are ordered at 77 K with a large hyperfine field; a smaller hyperfine field is associated with some magnetic clusters. This observation indicates that magnetic ordering with a high T_N is associated with a perovskite intergrowth phase; a $T_N \lesssim 77$ K is associated with other intergrowth clusters having fewer contiguous perovskite layers. There is no evidence of magnetic order in the region of pure La_2NiO_4.

Since the fraction of the sample at 4.2 K with a hyperfine field of 467 kOe is essentially the same as that showing magnetic order at 77 K, we assume that this represents a perovskite intergrowth, presumably at the surface of this sample. The existence of a second magnetic phase makes the spectrum at 77 K complex, especially as the remaining sample contains, at 4.2 K, paramagnetic regions that coexist with magnetically ordered regions having a T_N near 77 K. The fitting procedure used, which involves a static ($\tau_R > 10^{-7}$ s) nuclear configuration for all nuclei, and the large overlapping of the spectra do not allow great accuracy for the Mössbauer parameters, IS, QS, and the relative intensities, especially at 77 K.

About 11% of the cobalt in the sample remains paramagnetic even at 4.2 K, while the hyperfine fields associated with the magnetically ordered material are uniformly high.

A plausible model for these complex results is the following.

(a) Cobalt substitutes for nickel as high-spin Co^{3+} with a decided site preference for perovskite intergrowth layers.

(b) In pure, stoichiometric La_2NiO_4, a CDW in the $\sigma^*_{x^2-y^2}$ band sets in below $T_t \approx 200$ K to suppress long-range magnetic order, even though localized d_{z^2} spins are present, as previously suggested.[2]

(c) Nonstoichiometry, impurities, and perovskite intergrowth represent defects that lower T_t; antiferromagnetic order is stabilized where a $T_N > T_t$ occurs.

(d) Intergrowth regions containing several contiguous perovskite layers have a T_N in the range $77 < T_N < 300$ K and well above 77 K. These regions can be considered to function like a separate phase, and a $\tau_R > 10^{-7}$ s for this phase is established at 77 K.

(e) Regions containing intergrowths giving only pairs of contiguous perovskite layers have a $T_t < T_N \lesssim 77$ K; the strong single-ion anisotropy associated with high-spin Co^{3+} ions may enhance somewhat the T_N for long-range ordering and lengthen τ_R in domains of short-range ordering, but not significantly. The more highly doped $^{57}Fe:La_2NiO_4$ sample appears to have a similar $T_N \lesssim 77$ K for essentially all of the material.

(f) At 4.2 K, the ^{57}Co:La$_2$NiO$_4$ sample contains, in addition to the intergrowth phase ordered magnetically at 77 K, another magnetically ordered phase ($T_N > T_t$) coexisting with a paramagnetic phase ($T_t > T_N$). Since intergrowth layers tend to attract both Co^{3+} ions and Ni^{3+} ions, the crystalline defects are not uniformly distributed. It is therefore logical to conclude that the magnetically ordered regions contain intergrowths and the paramagnetic regions do not. This deduction is consistent with an apparently high QS value for the paramagnetic phase.

A few additional observations are worthy of comment.

(a) The data are too complex to permit identification of two distinguishable isomer shifts in the nonmagnetic regions at 4.2 K.

(b) A high-spin Co^{3+} ion in an octahedral site distorted to tetragonal symmetry with $c > a$ will carry a giant first-order single-ion anisotropy and magnetostriction that contributes to QS below T_N.

(c) The hyperfine field at 4.2 K is a measure of the strength of the interatomic exchange as well as of the electronic density in the nucleus of ^{57}Fe. The Fe—O distance is smaller in the perovskite blocks, which produces a greater covalency and therefore a smaller hyperfine magnetic field. The perovskite $LaNiO_3$ is metallic and without spontaneous magnetism.

(d) We have argued that the room-temperature spectra provide a measure of the distribution of dopant ions between regular and intergrowth sites. The apparent change in dopant-ion distribution on lowering the temperature cannot represent an actual change in the distribution; it reflects the fact that magnetic order does not appear uniformly through the sample. Comparison of the room-temperature and 4.2 K data shows about $66 \sim 68\%$ Fe^{3+} in regular sites in the absorber (Table I). In the source experiment, the situation remains complex at 4.2 K because of the coexistence of paramagnetic and magnetically ordered regions.

(e) In order to get accurate fits of the low-temperature spectra, it has been necessary to use a large distribution of magnetic fields (see Tables I and II). This fact corroborates the assumption of an inhomogeneous distribution of the ^{57}Co and ^{57}Fe environments in the two samples.

IV. CONCLUSIONS

Mössbauer absorption spectroscopy on ^{57}Fe:La$_2$NiO$_4$ at 297 K is able to distinguish Fe^{3+}-ion impurities in three different types of Ni sites, and these could be assigned to regular-site and intergrowth-site positions. Therefore we may conclude that our sample contained a significant concentration of intergrowth defects in addition to the iron impurities.

At 4.2 K, a hyperfine magnetic field of 450 ± 25 kOe provide direct evidence of long-range magnetic order throughout the sample. Long-range magnetic order is consistent with the absence of any evidence for the CDW below 200 K postulated for stoichiometric La_2NiO_4.[2]

Mössbauer emission spectroscopy on ^{57}Co:La$_2$NiO$_4$ has permitted observation of bulk material containing only small concentrations of Co impurities.

From the room-temperature emission spectrum, the cobalt can be assigned to the same substitutional positions as those found for iron from the absorber spectrum. However, the cobalt distribution over these sites is quite different from the iron distribution, and this follows from the different method of doping the samples. The spectrum at 77 K shows the presence of a magnetically ordered phase having a $T_N \gg 77$ K. This phase could be assigned to an intergrowth with multiple contiguous perovskite layers. At 4.2 K, a paramagnetic spectrum associated with regular sites coexists with two superimposed magnetic phases established at 77 K. The second magnetic phase had a $T_N \lesssim 77$ K, which is similar to the magnetic phase found in the ^{57}Fe:La$_2$NiO$_4$ sample.

We conclude that the postulated CDW is suppressed by lattice defects in only a part of the ^{57}Co:La$_2$NiO$_4$ even though we could not resolve two different paramagnetic cobalt impurities at 4.2 K. To this extent, our evidence for a CDW in stoichiometric La_2NiO_4 remains only indirect.

ACKNOWLEDGMENTS

One of us (J.F.) would like to acknowledge support of this research by CIRIT (Generalitat de Catalunya, Spain).

---

[1] J. B. Goodenough and S. Ramasesha, Mater. Res. Bull. **17**, 383 (1982).

[2] K. K. Singh, P. Ganguly, and J. B. Goodenough, J. Solid State Chem. **52**, 254 (1984).

[3] P. Ganguly, S. Kollali, C. N. R. Rao, and S. Kern, Magn. Lett. **1**, 107 (1980).

[4] G. A. Smolensky, V. A. Bokov, S. A. Kizaev, E. I. Maltzev, G. M. Nedlin, V. P. Plakhty, A. G. Tutov, and V. M. Judin in *Proceedings of the International Conference on Magnetism, Nottingham, 1964* (Institute of Physics, London, 1965), p. 354.

[5] J. L. Soubeyroux, P. Courbin, L. Fournes, D. Fruchart, and G. Le Flem, J. Solid State Chem. **31**, 313 (1980).

[6] G. Demazeau, M. Pouchard, M. Thomas, J. F. Colombet, J. C. Greneir, L. Fournes, J. L. Soubeyroux, and P. Hagenmuller, Mater. Res. Bull. **15**, 451 (1980).

[7] J. Drennan, C. P. Tavares, and B. C. H. Steele, Mater. Res. Bull. **17**, 621 (1982).

[8] G. K. Wertheim, Phys. Rev. **124**, 764 (1961); W. Triftshauser and P. P. Craig, *ibid.* **162**, 274 (1967); H. N. Ok and J. G. Mullen, *ibid.* **168**, 563 (1968); T. Harami, J. Loock, E. Huenges, J. Fontcuberta, X. Obradors, J. Tejada, and F. Parak, J. Phys. Chem. Solids **45**, 181 (1984).