Local Coordination of Low-Spin Ni^{3+} Probes in Trigonal $LiAl_yCo_{1-y}O_2$ Monitored by HF-EPR

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Received: November 26, 2003

The local coordination of low-spin Ni³⁺ probes in trigonal LiAl_yCo_{1-y}O₂ was studied using high-frequency EPR spectroscopy. This technique allows distinguishing between two types of Ni³⁺ ions: Ni³⁺ ions in trigonal crystal field (²E_g ground state) and Ni³⁺ ions in tetragonal crystal field (²A_{1g} ground state). When a Ni³⁺ ion is in a uniform Co environment, the orbitally degenerate state for Ni³⁺ is preserved and the EPR spectrum of the ground vibronic doublet state can be observed (intermediate Jahn–Teller effect). The value of g₁ decreases as the mean M–O bond is contracted. The local tetragonal distortion can be observed for Ni³⁺ ions located in a mixed Co_{6-y}Al_y environment. Along the progressive replacement of Co by Al, the strength of the crystal field for Ni³⁺ increases gradually and the extent of the tetragonal distortion displays a tendency to increase. The maximum effect of Jahn–Teller distortion is achieved when the Ni³⁺ ion falls in a pure Al environment.

1. Introduction

The layered solid solutions of LiCoO₂ with α -LiAlO₂ are of interest as cathode materials for lithium ion batteries since they are able to deintercalate/intercalate lithium reversibly at a potential higher than 4 V.^{1,2} The reversible electrochemical extraction of Li takes place concomitantly with the reversible oxidation of Co³⁺ to Co⁴⁺. Irrespective of the fact that the Al dopant does not participate in the electrochemical reaction, it has been found that the progressive replacement of Co by Al leads to a smooth increase of the potential where Li is extracted.¹⁻⁴

These materials have also been shown to be interesting for NMR and EPR spectroscopic studies.^{2,5} Using ²⁷Al MAS NMR spectroscopy, the novel aspect of the ²⁷Al NMR chemical shift has been found for these materials. The ²⁷Al MAS NMR spectra collected by using a high spinning speed in a high magnetic field (11.7 T) display a regular chemical shift from 62.5 to 20 ppm with an increment of 7 ppm along the substitution of Al for Co.5 The observed changes in the ²⁷Al NMR chemical shift have been attributed to the Co nucleus located in the second metal shell. Moreover, the distribution of the components in the complex profile of the NMR spectrum has been shown to obey the statistical distribution of the Co/Al nucleus. This effect is specific for the Co nucleus only. For example, the Ga nucleus characterized by a high quadrupolar magnetic moment and also located in the second coordination sphere has no significant effect on the chemical shift of ²⁷Al.⁶

Nickel is found to replace Co^{3+} ions from the CoO₂ layers, thus forming $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ solid solutions in the whole concentration range: $0 \le x \le 1$. ^{7,8} For layered $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ compositions, it is well-known that Ni and Co adopt low-spin configurations: $(t_{2g})^6(e_g)^1$ and $(t_{2g})^6$ respectively. The diamag-

netic character of LiAl_vCo_{1-v}O₂ permits exploring the effect of the nontransition metal neighbors on the electronic structure of transition metal ions in the honeycomb layer using Ni³⁺ spin probes. Due to the high sensitivity of the EPR spectroscopy in the X-band, even small amounts of paramagnetic Ni³⁺ ions replacing Co^{3+} in the diamagnetic LiAl_vCo_{1-v}O₂ can be detected by EPR (less than 0.05%, which is the common impurity content for cobalt salts without special purification).² In the CoO₂ layers, the Ni³⁺ spin probes adopt the low-spin configuration with a double degenerate ground state, which is Jahn-Teller unstable in a trigonal symmetry. Therefore, the EPR spectrum of Ni³⁺ is dominated by the Jahn-Teller effect.9 When Al substitutes for Co in LiCoO₂, a strong change in the EPR spectrum of Ni³⁺ spin probes has been detected. For LiAl_vCo_{1-v}O₂ obtained by a solid-state reaction, the EPR spectrum of Ni³⁺ displays several signals with tetragonal symmetry.² However, the low resolution of the EPR spectrum of Ni³⁺ recorded at 9.23 GHz (X-band) makes their interpretation difficult.² The requirement to obtain EPR spectra with a better resolution necessitates using highfrequency and high-field EPR spectroscopy (HF-EPR). This technique has been shown to provide invaluable information on the electronic structure of transition metal complexes.¹⁰⁻¹² For systems with $S = \frac{1}{2}$, HF-EPR allows resolving small g tensor anisotropy,¹² whereas for systems with integer spin, the higher field used permits observation of the EPR spectrum of a system denoted as "EPR-silent" in conventional X-band spectroscopy.¹³ Recently, HF-EPR technique has been successfully applied to study in more details the electronic structure of Ni^{3+} in tetragonal La₂Ni_{0.5}Li_{0.5}O₄⁻¹⁴ and trigonal LiGa_yCo_{1-y}O₂ solid solutions.⁶ Although the bonding properties of Ni^(III)O₆polyhedra in fluorides and oxides with perovskite- and K₂NiF₄type structures has been the subject of the intensive studies by conventional EPR spectroscopy,15-20 little work has been done on Ni³⁺ in layered oxides with trigonal crystal structures.

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Figure 1. X-band (9.23 GHz) EPR spectra of Ni³⁺ spin probes in LiAl_yCo_{1-y}O₂.

Here we extend the EPR study to the local coordination of Ni^{3+} in trigonal LiAl_yCo_{1-y}O₂ solid solutions by using high-frequency EPR (HF-EPR). This technique permits more precise differentiation between the Ni³⁺ ions having slightly different *g* values. Solid solutions between LiCoO₂ and LiAlO₂, in which Co and Al are statistically distributed within the layers as shown by ²⁷Al NMR,⁵ were prepared by the citrate precursor method.

2. Experimental Section

Samples of LiAl_vCo_{1-v}O₂ with $0 \le y \le 0.8$ were prepared by the citrate precursor method as described elsewhere.⁵ This method consists of thermal decomposition of Li-Co-Al citrate complexes. Lithium-cobalt-aluminum citric acid compositions were obtained by dissolution of Li2CO3, CoCO3, and Al(NO3)3. 9H₂O in aqueous solutions of citric acid (0.1 M) at 80 °C. The ratio between the components was as follows: Li:(Co + Al): Cit = 1:1:1 and Al:(Co + Al) = y, $0 \le y \le 1.0$. After complexation, the solution obtained was cooled to room temperature, then frozen instantly with liquid nitrogen, and dried in a vacuum (20-30 mbars) at -20 °C with an Alpha-Crist Freeze-Dryer. After drying, the solid residues were decomposed at 450 °C with a heating rate of 1°/min and were further heated at 800 °C for 24 h. The layered modification of LiAlO₂ was prepared by a solid-state reaction between boehmite (Al.O.OH doped with Ni, Ni/Al = 0.6%) and Li₂CO₃ at 600 °C for 30 h in O₂ atmosphere.

The lithium content of the samples was determined by atomic absorption analysis. The total amount of cobalt was determined complexometrically and by atomic absorption analysis. The mean oxidation state of cobalt was determined by an iodometric titration.

Electron paramagnetic resonance (EPR) measurements at 9.23 GHz (X-band) were carried out in a ERS 220/Q spectrometer within the temperature range of 85–410 K. The *g* factors were established with respect to a Mn^{2+}/ZnS standard. The high-frequency EPR spectra were recorded on a single-pass transmission EPR spectrometer built in the High-Magnetic Filed Laboratory, Grenoble, France. The frequencies were changed from 95 to 345 GHz using Gunn diodes and their multipliers.

The detection of absorption was performed with an bolometer. The recording temperatures were varied from 5 to 300 K using a variable temperature insert (Oxford Instruments).

3. Results and Discussions

Figure 1 summarizes the X-band EPR spectra of Ni³⁺ spin probes in $LiAl_{v}Co_{1-v}O_{2}$ solid solutions as a function of the registration temperature. Above 300 K, the EPR spectrum of Ni³⁺ spin probes in Al-substituted LiCoO₂ consists of a single line with Lorentzian shape and g factor insensitive toward the Al content in $LiCoO_2$ (g = 2.142). The single Lorentzian line with the same EPR parameters has already been detected in the EPR spectrum of low-spin Ni³⁺ in LiCoO₂. The dynamic Jahn-Teller effect for the ${}^{2}E_{g}$ orbital state is thought to be responsible for the appearance of the Lorentzian EPR line. On cooling to 85 K, the EPR spectrum of Ni³⁺ in LiCoO₂ remains as a single Lorentzian line, whereas the EPR signal from Ni³⁺ in Al substituted oxides undergoes a strong change. The single Lorentzian line is broken into several signals, the temperature of splitting being dependent on the Al-to-Co ratio (Figure 1). Below 230 K, a tetragonally asymmetric signal with $g_{\perp} = 2.1935$ and $g_{||} = 2.0535$ is superimposed on the single Lorentzian line for slightly doped LiAl_yCo_{1-y}O₂, (0.05 $\leq x < 0.25$). In the EPR notation, the tetragonal signal corresponds to a tetragonally elongated "static" Jahn-Teller Ni³⁺ configuration. The g-tensor of the tetragonal signal detected at 85 K displays a poor dependence on the amount of Al substituted for Co. By increasing the Al content, the anisotropic signal becomes more complex. Below 270 K, a new anisotropic signal grows in intensity in addition to the tetragonally asymmetric signal. At 85 K, the single symmetrical line still remains in the central part of the EPR spectra of LiCo1-vAlvO2 and its intensity decreases with the Al content (Figure 1). Contrary to the hightemperature Lorentzian signal, the low-temperature symmetrical signal displays a dependence of the g factor on the Al content: the g factor decreases along the Al substitution. The overlapping of the signal with tetragonal symmetry with the single Lorentzian line has been observed at the EPR spectrum of Ni³⁺ spin probes in Ga substituted LiCoO₂, i.e., LiGa_vCo_{1-v}O₂ matrix.⁶ However,



Figure 2. EPR spectra recorded at 9.23 and 115 GHz of Ni^{3+} spin probes in LiAl_yCo_{1-y}O₂, Ni/(Al + Co) = 0.006. For the sake of comparison, thin lines correspond to the spectra of undoped oxides.

the important difference between the EPR spectra of Ni³⁺ in both LiAl_yCo_{1-y}O₂ and LiGa_yCo_{1-y}O₂ matrixes is manifested in the low-magnetic field region. For a Ga-rich composition, X-band EPR spectra exhibit a new signal with $g \approx 5$ ascribable to high-spin Ni³⁺ located near defect sites.⁶ Since this signal is not detected for Al substituted LiCoO₂, one may conclude that these defects are specific for the Ga-substituted oxides.

Below 80 K, a further change in the EPR profile of Ni³⁺ takes place. To improve the resolution of the EPR spectrum, HF-EPR was undertaken. However, due to the lower sensitivity of the HF-EPR technique (single-pass technique) as compared to the conventional X-band EPR spectrometer, a higher spin concentration is needed. That is why the oxides have additionally been doped with Ni with a concentration of Ni/(Co + Al) = 0.006. In this case, the signal in the X-band EPR spectrum is broadened, but the EPR profile is preserved (Figure 2). Moreover, the crystal structure parameters of Ni doped LiAl_yCo_{1-y}O₂ remain the same.

At 5 K, Figure 3 compares the EPR spectra of Ni³⁺ in LiAl_yCo_{1-y}O₂ recorded at 115 GHz. The EPR spectrum of Ni³⁺ in pure LiCoO₂ consists of an anisotropic doublet and a nearly symmetric single line in the central part. According to our previous X- and Q-band EPR studies on Ni doped LiCoO₂, the anisotropic doublets originate from the ground vibronic doublet state, whereas the single line can be assigned to an excited vibronic singlet and/or relaxation averaged singlet.⁹ This feature is typical for ²E_g ions with a weak to moderate Jahn–Teller coupling (intermediate Jahn–Teller effect).^{21,22} The corresponding *g* factors are

$$g_{+} = g_{1} + qg_{2}f(\bar{\alpha}) \tag{1}$$

$$g_{-} = g_1 - qg_2 f(\bar{\alpha}) \tag{2}$$

Here, q is the vibronic reduction factor, $f(\bar{\alpha})$ is the function of the mean angle, $\bar{\alpha}$, between the vectors of the random strains and the external magnetic field, and $g_2 = g_1 - 2.0023$ is the contribution of the orbital magnetic moment to the overall magnetic moment.

In addition, a signal with a tetragonal symmetry can also be resolved in the EPR spectrum of Ni^{3+} ions in LiCoO₂ (Figure 3). This feature is characteristic of the "quasistatic" Jahn–Teller effect: random strengths permit coupling of the excited A₁-(A₂) vibronic levels to the ground vibronic doublet state, thus



Figure 3. EPR spectra at 5 K of Ni³⁺ spin probes in LiAl_yCo_{1-y}O₂, Ni/(Al + Co) = 0.006. EPR spectra were recorded at 115 GHz. Thin lines correspond to the simulated signal with tetragonal symmetry. The signal due to Ni³⁺ in trigonal crystal field is indicated in the experimental spectrum of LiCoO₂.

leading to a new set of vibronic basis states whose vibrational part represents a distortion along one of the cubic 4-fold axes. The transition from intermediate to quasistatic Jahn–Teller for Ni^{3+} substituted for Co^{3+} in the CoO_2 layers is associated with the increased role of the random lattice strains due to lattice inperfections.^{22,23}

When Al substitutes for Co, there is a strong change in the EPR profile of Ni³⁺ spin probes (Figure 3). For slightly substituted oxides, the spectrum exhibits a tetragonal symmetry with a g tensor depending on the amount of Al substituted for Co (Table 1). This behavior is typical of the static Jahn-Teller effect. By increasing the Al amount, the perpendicular complex envelope is split into several components, whereas the changes in the parallel envelope are less obvious. For the sample with 50% of Al, the perpendicular envelope can be presented as a sum of the perpendicular components of signals characteristic of the two end compositions, $LiAl_{0.1}Co_{0.9}O_2$ and $LiAl_{0.8}Co_{0.2}O_2$. For the end LiAlO₂ composition, the EPR spectrum consists of a tetragonal symmetry signal with a small anisotropy in the perpendicular region. By increasing the recording temperature, the perpendicular components are broadened and, finally, coalesce into one nearly symmetrical signal due to the dynamic Jahn-Teller effect (Figure 4, Figure 1). There is a decrease in the value of g_{\perp} when the Al content increases (Table 1). In all cases, g_{\perp} is greater than g_{\parallel} , indicating that the Ni³⁺ ions are in a tetragonally elongated octahedron with an ²A_{1g} ground state. Irrespective of the fact that the LiCoO₂ host provides a trigonally distorted site, the observation of Ni³⁺ in tetragonal symmetry can be understood in terms of local tetragonal distortion not affecting the collective trigonal symmetry. Moreover, the local tetragonal distortion of the crystal site in a trigonal symmetry host has also been found for NiO₆ in trigonal LiNiO₂ based on Ni K-edge EXAFS analysis.24

The values of g_{\parallel} and g_{\perp} can be expressed by²⁵

$$g_{||} = g_{e} + 2(\xi/\delta)^{2}$$
 (3)

$$g_{\perp} = g_{\rm e} + 3\xi (1.38/E_3 + 0.62/E_4) + 2(\xi/\delta)^2 \qquad (4)$$

The deviation of g_{\parallel} from the g factor of the free electron (g_e)

TABLE 1:	g Tensor	for Low-Spin	Ni^{3+} in 1	LiALCo1O2	Hosta
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	Ni ³⁺ in tetragonal crystal field		Ni ³⁺ in trigonal crystal field			
matrix	g_{\perp}	gII	g_1	qg_2	r _{av} , Å	$r_{\rm ax}/r_{\rm eq}$
LiCoO ₂	2.1759	2.0739	2.1415	0.0333	1.932	
$LiCo_{0.9}Al_{0.1}O_2$	2.1967	2.0394	2.1393	0.0437	1.931	
	2.1868	2.0394				
$LiCo_{0.5}Al_{0.5}O_2$	2.2002	2.0405	2.1344	0.0439	1.927	
	2.1924	2.0405				
	2.1856	2.0396				
	2.1768	2.0396				
$LiCo_{0.2}Al_{0.8}O_2$	2.1844	2.0391	2.1280	0.0422	1.910	
	2.1721	2.0391				
LiAlO ₂	$g^{1}=2.1700$	2.0379			1.926	
	$g^2 = 2.1610$					
La2Li0.5Ni0.5O4 ^[19]	2.253	2.015			1.95	1.20
$NaNiO_2[21]$	2.283	2.030			1.99	1.12
LaSrAl _{0.90} Ni _{0.10} O ₄ ^[20]	I - 2.212	2.043			1.92	1.04
	II – 2.253	2.043				
	III: $g^1 = 2.344$	$g^3 = 2.043$				
	$g^2 = 2.22$					
LaSrGa _{0.93} Ni _{0.07} O ₄ ^[19]	ž.227	2.044			1.99	1.07
	2.250	2.044				
Ni ³⁺ in cubic MgO [28]			2.1685	0.06	2.106	

^a The mean M–O bond length, the extent of tetragonal distortion expressed by the ratio between two long and four short bond lengths (r_{ax}/r_{eq}).



Figure 4. Temperature variation of the EPR spectra of Ni^{3+} in $LiAl_{0.5}Co_{0.5}O_2$ (left) and $LiAl_{0.8}Co_{0.2}O_2$ (right). EPR spectra were recorded at 115 and 285 GHz, respectively.

results from the doublet-quartet energy separation, δ , whereas the doublet-quartet energy separation and the ligand-field energies of the transitions ${}^{2}A \rightarrow {}^{2}{}_{a}T_{2}$, ${}^{2}{}_{b}T_{2}$, contribute to the g_{\perp} value. In terms of Jahn-Teller stabilization, the low-spin configuration (doublet state) can lower its energy with respect to the high-spin configuration (quartet state) by increasing the tetragonal elongation. This means that the g_{\parallel} value provides information on the extent of the tetragonal distortion. Table 1 gives the g tensor values of Ni³⁺ in a tetragonal-symmetry host (e.g., LaLi_{0.5}Ni_{0.5}O₄, LaSrAl_{1-x}Ni_xO₄, and LaSrGa_{1-x}Ni_xO₄ with the K₂NiF₄-type structure and the monoclinic layered structure NaNi O_2), ^{19,20,26,27} where the extent of tetragonal distortion of the Ni^(III)O₆ octahedron is determined by diffraction methods. (The extent of the tetragonal distortion is expressed by the ratio of the axial and equatorial bonds: r_{ax}/r_{eq} .). As the extent of the tetragonal distortion increases, the g_{\parallel} value tends to g_{e} . The increase in the g_{\perp} value reveals the weakness in the crystal field due to the increase in the Ni-O bond length.

The comparison of the g-tensor for Ni³⁺ in a tetragonalsymmetry host with that for Ni³⁺ in a layered LiAl_yCo_{1-y}O₂host shows that the extent of tetragonal distortion for the Ni³⁺O₆ octahedron tends to increase slightly with the Al content and reaches $1.12 > r_{ax}/r_{eq} \ge 1.08$ (Table 1). A similar tetragonal elongation for the Ni³⁺O₆ octahedron has been found for Ga substituted LiCoO₂: $r_{ax}/r_{eq} \ge 1.08.^{6}$ Using Ni K-edge EXAFS studies of nearly stoichiometric $Li_{1-\delta}Ni_{1+\delta}O_2$ ($\delta \approx 0.02$), the extent of local tetragonal distortion for the Ni(III)O octahedron has been evaluated: $r_{\rm ax}/r_{\rm eq} = 1.09.^{24}$ The close tetragonal elongation estimated for Al- and Ga-substituted LiCoO₂ and $Li_{1-\delta}Ni_{1+\delta}O_2$ suggests that the Jahn–Teller effect for Ni³⁺ in layered lithium transition metal oxides is limited by the rigidity of the close packed structure. The decrease in g_{\perp} with increasing Al content means that the Ni-O bond becomes more covalent, i.e., the strength of the crystal field increases. The discrete strengthening of the crystal field of Ni³⁺ can be associated with the effect of the first metal neighbors in the layer. The metal layers of trigonal LiMO₂ are composed of edge sharing MO₆ octahedra, where every Ni³⁺ ion in the layer has 6 metal neighbors at a distance a (a, unit cell parameter). Figure 5 shows the dependence of the g tensor of Ni^{3+} on the number of Al neighbors in the first metal shell. The relation between the electronic structure and the g tensor for low-spin Ni^{3+} (eq 1) indicate that the strength of the crystal field of Ni³⁺ increases gradually with the number of Al in the first metal sphere, but the extent of the tetragonal distortion is limited by the host matrix. The discrete changes in the strength of the crystal field of Ni³⁺ along the Al substitution bears resemblance with the regular chemical shift of the ²⁷Al nucleus (from 62.5 to 20 ppm) observed in the NMR spectra of the LiAl_vCo_{1-v}O₂ solid solution.⁵ The effect of the metal neighbors on both the EPR



Figure 5. Values of the g tensor for Ni^{3+} in tetragonal crystal field versus the number of Al included in the next metal [Al_nCo_{6-n}] environment.

spectra of Ni³⁺ and the ²⁷Al NMR spectra is the most interesting experimental finding, which deserves further theoretical description. It is worth mentioning that metal neighbors in oxides with a K₂NiF₄-type structure have been shown to induce either tetragonal elongation or tetragonal compression of the Ni^(III)O₆ octahedra.^{17,29} A NiO₆ distortion in LaSrAl_{1-x}Ni_xO₄ due to the preferential coordination of Sr²⁺ or La³⁺ has also been proposed to explain the doubling of the perpendicular component of the g tensor with constant parallel component.²⁰

The second feature of the low-temperature HF-EPR spectra of Ni³⁺ in Al substituted oxides is the appearance of the signal due to moderate JT coupling (Figure 3). For slightly substituted oxides, this signal is barely detected, whereas a well-resolved signal is observed with the Al rich oxide. The doublet signal characteristic of Ni³⁺ in LiCoO₂ is not observed for Ni³⁺ in layered LiAlO₂. The value of g_1 decreases as the Al content increases. As in the case of pure LiCoO₂, this signal can be assigned to Ni³⁺ in a trigonally distorted crystal field, i.e., to Ni³⁺ ions in ²E_g ground state. For comparison, Table 1 also gives the EPR parameters for the ground vibronic state of Ni³⁺ dopants in a MgO matrix with a cubic symmetry.²⁸ There is a dependence of the value of g_1 on the mean M–O bond length determined by XRD technique.

The observation of two types of Ni³⁺ ions in a trigonal $LiAl_{v}Co_{1-v}O_{2}$ host can be rationalized if we take into account the effect of the metal neighbors. When Co³⁺ ions surround Ni³⁺ only in the metal layer, the local trigonal symmetry of the host site is preserved and Ni^{3+} in E_g ground state is detected. The progressive changes in the metal coordination sphere from Co^{3+} to Al^{3+} along with the substitution are, on one hand, responsible for the local tetragonal distortion of the host site and, on the other, contribute to the electronic structure of Ni³⁺. The first metal coordination sphere becomes important and the nature of the atom in this position will lead to further differentiation of Ni3+ in a tetragonal crystal field. The maximum effect of Jahn-Teller stabilization is achieved when Ni³⁺ is in pure Al surrounding.

4. Conclusions

The use of HF-EPR spectroscopy allows us to distinguish between Ni^{3+} ions in ${}^{2}E_{g}$ and ${}^{2}A_{1g}$ ground states. When the Ni^{3+} ion is in a uniform Co environement, the orbitally degenerate

state for Ni³⁺ is preserved and the EPR spectrum of the ground vibronic doublet state can be resolved (intermediate Jahn-Teller effect). The value of g_1 decreases as the mean M–O bond is contracted. The local tetragonal distortion can be observed for Ni^{3+} ions located in mixed $Co_{6-\nu}Al_{\nu}$ environment. The strength of the crystal field for Ni³⁺ increases gradually, and the extent of the tetragonal distortion shows a tendency to increase along the progressive replacement of Co by Al.

Acknowledgment. E.Zh. and R.S. are indebted to the National Science Fund of Bulgaria (Contract No. Ch1304/2003) for financial support. The authors acknowledge financial support from MCyT (Contract MAT2002-00434) and Programa Ramón y Cajal. R.S. is grateful to the EC for a grant within the "Access to Research Infrastructure action of the Improving Human Potential Program"-European Community having enabled her to perform the high-frequency EPR measurements at a High Magnetic Field Laboratory in Grenoble, France. The authors are very grateful to Dr. Anne-Laure Barra (High Magnetic Field Laboratory, Grenoble) for her help.

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