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EMISSION MÖSSBAUER STUDY OF ^{57}Fe IN ^{57}Ni-LABELLED NICKEL (II) OXALATE DIHYDRATE

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Abstract—Emission Mössbauer spectroscopy of ^{57}Fe generated from the ^{57}Ni → ^{57}Co → ^{57}Fe double decay in ^{57}Ni-labelled Ni(II)oxalate is compared with previous results obtained in the corresponding ^{57}Co-doped compound. In agreement with the energetics of ^{57}Ni decay, recoil of nucleogenic ^{57}Co atoms is observed at 90 K in some 60% of the nuclear events. This results in highly perturbed Fe states. Total annealing is observed at room temperature. A stabilization scheme of the ^{57}Fe nucleogenic species is described by applying a "double self-radiolysis model" adjusted to account for the cumulative effects of the successive nuclear transitions. Semi-theoretical estimates of the distribution of the intermediate ^{57}Co atoms and of the various ultimate ^{57}Fe species are proposed.

Keywords: ^{57}Ni decay, recoil, electron capture after-effects, nickel(II) oxalate dihydrate, Mössbauer spectroscopy.

1. INTRODUCTION

In the present work, the physico-chemical state of nucleogenic ^{57}Fe atoms generated by the cumulative decays of ^{57}Ni ($T = 36$ h; 43% β^+, 57% EC) and ^{57}Co ($T = 272$ *d*; 100% EC) in ^{57}Ni-labelled nickel(II) oxalate dihydrate is investigated *in situ* by means of emission Mössbauer spectroscopy and compared with the behaviour of the corresponding ^{57}Co-doped compound, where ^{57}Fe results from the single electron capture decay of ^{57}Co.

Such cumulative effects have been previously studied in a nickel metal host matrix [1], where recoil of the nucleogenic atoms is evident as long as the ^{57}Ni decay has been achieved at a low temperature (77 K). This result was quite in agreement with the energetics of the ^{57}Ni decay. A detailed analysis of the ^{57}Ni and ^{57}Co decay schemes (based on [2]) has been presented in the above-mentioned paper. Since a new compilation of the relevant nuclear data (based on a total decay energy, $Q = 3265$ keV [3]) is now available [4], we report hereafter (Table 1) some characteristic values of the recoil energies (E_R) associated with the individual processes of these nuclear transitions, which differ slightly from the previously mentioned ones, although major changes are not involved.

As shown by these data, the recoil energies associated with the first nuclear decay often lie above the typical displacement threshold energy values accepted for crystalline materials ($E_d = 25$ eV), whereas no displacement can occur during the next disintegration of ^{57}Co into ^{57}Fe. In Ni(II) oxalate dihydrate, recoil of the nucleogenic ^{57}Co implies the breakage of six Ni–O bonds, whose individual dissociation energy has been estimated at 4 eV in NiO [5], but lower values (2–3 eV) have been observed in various chelated complexes [6, 7]. Displacement threshold energies between 15 and 25 eV can thus be considered as reasonable.

As indicated in Table 1, the maximum recoil energy available for the ^{57}Co atoms amounts to 35 eV (14%) and E_R is larger than 25 eV for some 60% of the nuclear events. In any case, E_R exceeds the lower limit of 15 eV, independently from the decay mode of the ^{57}Ni parent atom. Besides, whereas conducting materials like metallic nickel are known to be free from any electronic or self-radiolytic effect, the situation is much more complicated in coordination compounds with polyatomic ligands. In these systems, the electronic—related to the lattice characteristics—and radiolytic—related to the nature of the ligands—effects have to be taken into account. This is the reason why a previous study [8] was performed on the corresponding ^{57}Co-doped compound, which provided two main conclusions. Firstly, extra-stabilization of Fe^{3+} was observed in the nickel compound with respect to the corresponding compounds of other host cations (Co, Fe, Mn, Zn and Mg), and has been assigned to steric and thermodynamic factors. Secondly, the improvement of the self-radiolysis model allowed one to characterize three major Fe components in the emission spectra; two of them correspond to substitutional ferrous species either in a normal (Fe_N^{2+}), or in a perturbed (Fe_{AL}^{2+}) coordination sphere (due to electronic transfer between the radiolysed ligands and the iron ion), the third one corresponding to the aliovalent ferric state. These conclusions are essential to an understanding of what will happen in the ^{57}Ni-labelled compound, in order to enable us to show the poor influence of the former decay on the observed distribution of the ^{57}Fe nucleogenic species.

2. EXPERIMENTAL

The experimental methods used for the production of the ^{57}Ni activity and the synthesis of the

Table 1. Free-atom recoil energies (E_R) associated with the individual processes of ^{57}Ni and ^{57}Co decays

Parent isotope	Decay mode	Emitted particle	Energy (keV)	E_R (eV)	Intensity (%)
^{57}Ni	EC	ν	1338‡	16.8	13.1
(Q = 3265 keV)†	(57.1%)		1500	21.2	5.1
			1752	28.9	9.5
			1880	33.2	28.9
	β^+	β^+¶	≤324§	≤4.1§	0.5‖
	(42.9%)		≤485	≤6.9	0.9
			≤738	≤12.2	6.7
			≤865	≤15.3	34.8
		ν††	≤865	≤7.0	—
		$\beta^+ + \nu$‡‡	Σ ≤ 865	≤13.7§§	—
	EC/β^+	γ	127.4	0.15	16.6
			1377.6	17.9	80.0
			1757.5	29.1	6.1
			1919.4	34.7	13.6
^{57}Co	EC	ν	693‖‖	4.5	100
(Q = 836 keV)†	(100%)				
		γ	14.4	0.002	9.6
			122.1	0.14	85.9
			136.5	0.17	10.2
			692.0	4.5	0.2
		ce¶¶	≤135	≤1.5	—

† Q = total decay energy (from [3]).
‡For K-capture ($EC_L/EC_K = 0.1$).
§Maximum values of $E_{\beta+}$ and corresponding E_R.
‖Total intensity for β^+ decay to a given nuclear level (absolute intensity for 100 decays of ^{57}Ni).
¶Hypothesis of a neutrino emitted at rest.
††Hypothesis of a positron emitted at rest.
‡‡Sharing of energy between positron and neutrino.
§§Range of values depending on the angular correlation between the emission directions of both particles.
‖‖Mean value for K-, L- and M-electron captures.
¶¶Conversion electrons.

^{57}Ni-labelled dihydrated nickel(II) oxalates have been reported elsewhere [1]. The initial ^{57}Ni activity used in the present experiments is about 10 mCi (370 MBq), which yields about 50 μCi (1.8 MBq) of ^{57}Co. In order to prevent most of the recovery effects during the nuclear decay of ^{57}Ni into ^{57}Co, the initial ^{57}Ni-labelled sample was stored in liquid nitrogen for 15 days. Emission Mössbauer spectra were registered at low temperature (90 K) before and after having warmed the sample to room temperature (RT) during 2 days. A subsequent Mössbauer analysis was then also performed at RT. The experimental Mössbauer device and the data fitting procedure have both been described in the above-mentioned paper [8]. Resonance is observed here between the sample and a moving stainless steel absorber (310 SS, $\Gamma = 0.45 \pm 0.03$ mm s^{-1}) kept at RT. All the isomer shifts cited hereafter are relative to α-Fe metal at 295 K. The velocity sign in the emission spectra has been reversed to allow direct comparison between corresponding absorption and emission Mössbauer data.

3. RESULTS AND DISCUSSION

3.1. *Description and interpretation of the Mössbauer spectra*

Figure 1(a) shows the emission spectrum of ^{57}Fe generated from the ^{57}Ni → ^{57}Co → ^{57}Fe double decay, registered at 90 K after the ^{57}Ni decay at 77 K. A very rough analysis of these data would give two superimposed doublets with extremely large linewidths, corresponding, respectively, to Fe^{2+} ($\Delta = 2.32$ mm s^{-1}; $\Gamma = 1.32$ mm s^{-1}; 78%) and Fe^{3+} ($\Delta = 0.72$ mm s^{-1}; $\Gamma = 1.61$ mm s^{-1}; 22%). On the other hand, as illustrated in Fig. 1(b), the low-temperature spectrum obtained after the sample has been warmed-up to RT for 2 days presents a completely different shape. The initial line broadening has decreased drastically allowing the experimental data to be characterized much more easily. As shown by comparing Fig. 1(b)–(d) and 1(c)–(e) (and the related Mössbauer parameters of Table 2), the annealed ^{57}Ni-labelled sample actually behaves quite similarly to the previously investigated ^{57}Co-doped sample, at 90 K as well as at RT.

Referring to this analogy, the Mössbauer spectra of the annealed ^{57}Ni-labelled sample were resolved into three components assigned to two ferrous states, Fe^{2+}_N and Fe^{2+}_{AL}, respectively, and one ferric component, according to the above-mentioned interpretation of the results for the ^{57}Co-doped samples. As shown by comparison with the absorption Mössbauer parameters of ^{57}Fe in $^{57}Fe{:}NiC_2O_4 \cdot H_2O$ [9], as listed in Table 2, the normal ferrous state, Fe^{2+}_N, corresponds to substitutional $^{57}Fe^{2+}$ in a $^{57}Ni^{2+}$

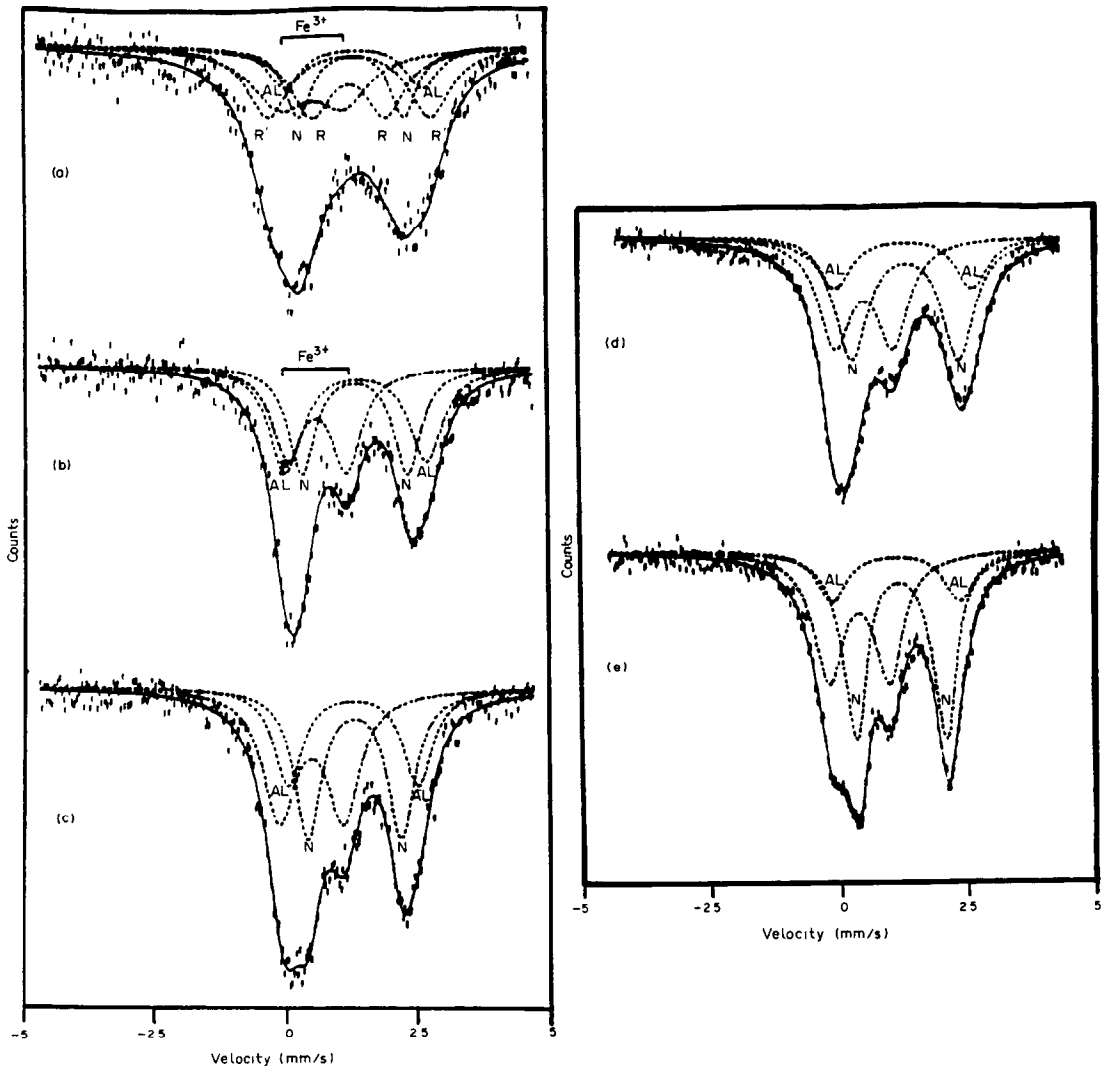

Fig. 1. ^{57}Fe emission Mössbauer spectra at 90 K (a), (b), (d) and 295 K (c), (e). (a), (b), (c): ^{57}Ni:$NiC_2O_4 \cdot 2H_2O$, (a) after decay at 77 K, before annealing; (b), (c) after annealing at 295 K; and (d), (e): ^{57}Co:$NiC_2O_4 \cdot 2H_2O$.

lattice site with a normal coordination sphere. The main difference between the related spectra of the ^{57}Co-doped and ^{57}Ni-labelled systems concerns the amount of the additional ferrous species, Fe^{2+}_{AL}, which is found to be significantly more abundant in the ^{57}Ni-labelled compound ($\simeq 30\%$) than in the ^{57}Co-doped sample ($\simeq 17\%$). Apart from the latter remark, the similarity observed between these spectra seems to indicate complete healing of the lattice after a 2 days' storage at RT. Consequently, the initial low-temperature spectrum of the ^{57}Ni-labelled compound can be considered as reflecting the occurrence of various highly perturbed nucleogenic species which are generated from the nuclear decay of the ^{57}Co recoil atoms in the lattice. Therefore, the components found in the spectrum of the annealed sample were substracted from the initial spectrum, by imposing on them the hyperfine parameters and relative intensities obtained at 90 K after annealing. This treatment results in showing two further ferrous doublets with large linewidths (0.84 and 1.09 mm s^{-1}) and a total intensity of about 50%, which are assigned to recoil species [Fe^{2+}_R; *RR* and *R'R'* in Fig. 1(a)]. The corresponding Mössbauer parameters are listed in Table 2.

A further comment can be made on the resulting ferric component of Fig. 1(a), which also appears as extremely broadened lines ($\Gamma = 1.37$ mm s^{-1}) and at a relative amount which is much larger with respect to the total substitutional iron ($Fe^{2+}_N + Fe^{2+}_{AL}$), than in the corresponding spectrum of the annealed sample. We think this suggests the occurrence of a certain amount of recoil Fe^{3+} species (Fe^{3+}_R), whose relative content can be estimated using the data of Table 3

Table 2. Mössbauer parameters of ^{57}Fe in ^{57}Ni-labelled, ^{57}Co-doped and ^{57}Fe-doped Ni(II) oxalate dihydrate

Compound	T_D† (K)	T_A† (K)	T_S† (K)	Δ‡ (mm s^{-1})	δFe§ (mm s^{-1})	Γ‖ (mm s^{-1})	I¶ (%)	Assignment
^{57}Ni:$NiC_2O_4 \cdot 2H_2O$	77	—	90	3.19	1.21	0.84	18	Fe_R^{2+}
				2.64	1.29	0.75	12	Fe_{AL}^{2+}
				2.02	1.24	0.62	12	Fe_N^{2+}
				1.65	1.21	1.09	32	Fe_R^{3+}
				1.22	0.48	1.37	26	Fe^{3+}
	77	295	90	2.62	1.29	0.75	34	Fe_{AL}^{2+}
				2.02	1.24	0.61	32	Fe_N^{2+}
				1.19	0.49	0.71	34	Fe^{3+}
	77	295	295	2.46	1.20	0.68	26	Fe_{AL}^{2+}
				1.78	1.23	0.62	36	Fe_N^{2+}
				1.22	0.41	0.77	38	Fe^{3+}
^{57}Co:$NiC_2O_4 \cdot 2H_2O$ [8]	—	—	90	2.64	1.22	0.76	18	Fe_{AL}^{2+}
				2.06	1.25	0.76	44	Fe_N^{2+}
				1.11	0.45	0.76	38	Fe^{3+}
	—	—	295	2.50	1.13	0.70	16	Fe_{AL}^{2+}
				1.76	1.19	0.55	46	Fe_N^{2+}
				1.18	0.40	0.68	38	Fe^{3+}
^{57}Fe:$NiC_2O_4 \cdot 2H_2O$ [9]	—	—	80	1.97	1.29	0.30	100	Fe_N^{2+}
	—	—	295	1.71	1.18	0.29	100	Fe_N^{2+}

† T_D = decay temperature (^{57}Ni → ^{57}Co); T_A = annealing temperature; T_S = Mössbauer source (^{57}Co) or absorber (^{57}Fe) temperature.
‡Quadrupole splitting (±0.05 mm s^{-1}).
§Isomer shift relative to α-Fe metal at 295 K (±0.05 mm s^{-1}).
‖Full-width at half-maximum (±0.05 mm s^{-1}).
¶Relative intensity of the iron component (±5%).

as follows:

in ^{57}Ni:$NiC_2O_4 \cdot 2H_2O$, after annealing:

$$(Fe)_{total} = Fe_N^{2+} + Fe_{AL}^{2+} + Fe_{N+AL}^{3+} = (Fe)_{N+AL} = 1.00 \quad (1)$$

$$\frac{Fe_{N+AL}^{3+}}{(Fe)_{total}} = 0.36 = \frac{Fe_{N+AL}^{3+}}{(Fe)_{N+AL}} \quad (\text{if } Fe_R^{3+} = 0); \quad (2)$$

in ^{57}Ni:$NiC_2O_4 \cdot 2H_2O$, non-annealed:

$$(Fe)_{total} = (Fe)_{N+AL} + (Fe)_R = 1.00 \quad (3)$$

$$(Fe)_R = Fe_R^{2+} + Fe_R^{3+} = 0.50 + Fe_R^{3+} \quad (4)$$

$$(Fe)_{N+AL} = (Fe)_{total} - (Fe)_R = 0.50 - Fe_R^{3+} \quad (5)$$

$$(Fe^{3+})_{total} = 0.26 = Fe_{N+AL}^{3+} + Fe_R^{3+}. \quad (6)$$

By equating the ratios of the mean relative proportions of Fe_{N+AL}^{3+} to the total substitutional Fe, $(Fe)_{N+AL}$, in both samples, one obtains, using eqns (2), (5) and (6),

$$\frac{Fe_{N+AL}^{3+}}{(Fe)_{N+AL}} = 0.36 = \frac{0.26 - Fe_R^{3+}}{0.50 - Fe_R^{3+}},$$

which results in $Fe_R^{3+} = 0.13$.

3.2. *Discussion*

Figure 2 presents the stabilization scheme of the different Fe nucleogenic species resulting from the successive decays of ^{57}Ni and ^{57}Co in ^{57}Ni:$NiC_2O_4 \cdot 2H_2O$. The main points are outlined below.

Table 3. Mean relative intensities (%) of ^{57}Fe nucleogenic species observed in the emission spectra of dihydrated oxalates

Nucleogenic species	^{57}Ni:Ni before annealing	^{57}Ni:Ni after annealing	^{57}Co:Ni [8]	^{57}Co:M (M = Fe, Co, Mn, Zn, Mg) [8]
Fe_N^{2+}	12	34	45	75
Fe_{AL}^{2+}	12	30	17	17
Fe_R^{2+}	50	—	—	—
$Fe_{N/AL}^{3+}$	26-x	36	38	8
$-Fe_N^{3+}$		25	33	—
$-Fe_{AL}^{3+}$		11	5	8
Fe_R^{3+}	x (estimated at 13)	—	—	—

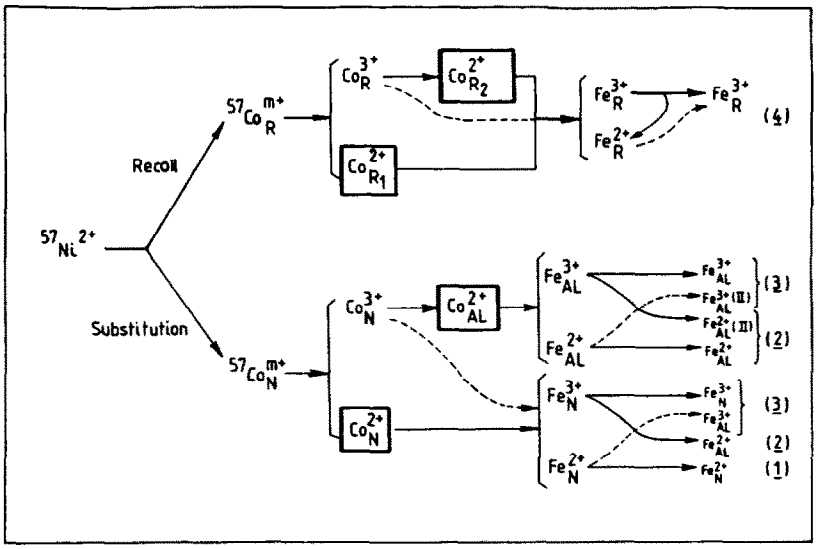

Fig. 2. Stabilization scheme of ^{57}Fe nucleogenic species resulting from the successive decays of ^{57}Ni and ^{57}Co in Ni(II) oxalate dihydrate.

(1) As concluded from the survey of the energetic aspects of the ^{57}Ni decay, if one admits a mean threshold energy for atomic displacement of 15–25 eV, recoil of nucleogenic ^{57}Co atoms during the first decay seems highly probable at least in 60% of the nuclear events. Displaced atoms are then located in strongly perturbed recoil sites (Co_R^{m+}), either as Co^{2+}, or as Co^{3+}. Because of the electronic excitation processes associated with the recoil displacement, the stabilization of the nucleogenic ^{57}Co in a reduced state (Co_R^{2+}) seems very likely. As the energy released during the second decay ($^{57}Co \rightarrow {}^{57}Fe$) is much smaller ($E \leqslant 4.5$ eV), some ultimate ^{57}Fe species could therefore be located in unusual configurations, and observed as recoil species (Fe_R^{2+} and Fe_R^{3+}) in a highly perturbed environment. In the present case, according to the former section, the total intensity of the recoil Fe atoms amounts to 63% (see Table 3). This result is quite compatible with the energetics of the ^{57}Ni decay and besides, it entirely agrees, not only with the aforesaid work on Ni metal [1], but also with a radiochemical study performed on ^{57}Ni-labelled nickel phthalocyanine [10, 11], which indicated a 37% retention.

(2) When no recoil occurs (if $E_R < E_d$) or when the atomic displacement is followed by return to the initial lattice site, the ^{57}Co nucleogenic atoms are found in substitutional positions. Their chemical state then results either from the consequences of the Auger effect which accompanies the ^{57}Ni electron capture decay, or from electronic excitations associated with the β^+-emission. In all cases, a large reduction in the yield of primary Co^{3+} is expected due to the strongly reducing environment, leading to an *additional* Co^{2+} species which is substitutional but has an altered coordination sphere (Co_{AL}^{2+}). When such effects are not operating, stabilization of substitutional Co_N^{2+} and Co_N^{3+}, with a normal coordination sphere, could be observed. At this stage, steric hindrance can also be invoked to predict the stabilization of Co atoms as Co^{2+} or Co^{3+}, but it should be noted that the influence of this factor will be smaller here than it would be in the simple $^{57}Co \rightarrow {}^{57}Fe$ transition, because of the smaller difference between the ionic radii of the ions concerned: Fe^{2+} (92 pm) > Co^{2+} (88.5 pm) > Ni^{2+} (83 pm) [12].

(3) When recoil occurs, as is observed in the low-temperature spectrum before annealing, the ^{57}Fe nucleogenic atoms finally detected by means of the Mössbauer effect arise from three kinds of ^{57}Co precursors: substitutional Co_N^{2+} or Co_{AL}^{2+} states, or recoil species which are mainly assumed to be in a divalent state, Co_R^{2+}. After the second electron capture decay, these atoms appear as four main species: Fe_N^{2+} (1), Fe_{AL}^{2+} (2), Fe^{3+} (3) and recoil species, Fe_R^{2+} and Fe_R^{3+} (4), according to the mean proportions of Table 3.

(4) Annealing at RT allows the recoil ^{57}Co atoms to re-enter their substitutional lattice site, in such a way that only two major precursors have to be considered: Co_N^{2+} and Co_{AL}^{2+}.

(5) Before as well as after annealing, since part of the Co^{2+} appears as Co_{AL}^{2+}, the occurrence of Fe_{AL}^{2+} observed after the subsequent decay now results from two different processes. The first one is the reduction of primary Fe_N^{3+} which originates either in Co^{2+} or in Co^{3+} in a normal substitutional site; the second one is the stabilization of Fe_{AL}^{2+} in its "primary" charge state, without any electron transfer, when resulting from the electron capture decay of $^{57}Co_{AL}^{2+}$, which already has a perturbed coordination sphere. On the other hand, the observed Fe_N^{2+} species arises only from a primary Co_N^{2+} state. This mechanism

explains the increase of the Fe^{2+}_{AL} amounts at the expense of Fe^{2+}_{N} in the emission spectra of the ^{57}Ni-labelled compound.

Using the data of Table 3, a semi-quantitative assessment of the charge state distribution can be achieved as follows:

in $^{57}Co:NiC_2O\cdot 2H_2O$:

$$^{57}Co^{2+}_{N} \xrightarrow{EC} \underset{(x)}{0.45}\ ^{57}Fe^{2+}_{N} + \underset{(y)}{0.17}\ ^{57}Fe^{2+}_{AL} + \underset{(z)}{0.38}\ ^{57}Fe^{3+};$$

in $^{57}Ni:NiC_2O_4\cdot 2H_2O$, after annealing:

$$^{57}Ni^{2+} \xrightarrow{EC/\beta+} m\ ^{57}Co^{2+} + n\ ^{57}Co^{3+}$$
$$\downarrow$$
$$m\ ^{57}Co^{2+}_{N} + n\ ^{57}Co^{2+}_{AL}$$
$$\downarrow$$
$$\underset{(x)}{0.34}\ ^{57}Fe^{2+}_{N} + \underset{(y)}{0.30}\ ^{57}Fe^{2+}_{AL} + \underset{(z)}{0.36}\ ^{57}Fe^{3+},$$

assuming total reduction of primary Co^{3+}.

Considering identical relative stabilization yields as Fe^{2+}_{N} in the ^{57}Co-doped and in the annealed ^{57}Ni-labelled samples, i.e.

$$0.34 = 0.45\,m,$$

this model accounts for an initial distribution of the ^{57}Co nucleogenic atoms as 75% Co^{2+}_{N} and 25% Co^{2+}_{AL} (which means 25% primary Co^{3+}).

This result agrees perfectly well with the conclusions drawn from previous radiochemical studies which dealt with the characterization of nucleogenic $^{57}Co^{n+}$ in various ^{57}Ni-labelled compounds. The investigation of several hexammine complexes [13, 14] and other chelates [15, 16] of Ni(II) indicated stabilization of some 60–80% Co^{2+} in the matrix.

A similar calculation can be performed to give a semi-theoretical estimate of the $^{57}Fe^{2+}_{AL}$ amount in the emission spectrum of the annealed-^{57}Ni-labelled compound. Assuming identical reduction yields of Fe^{3+} into Fe^{2+}_{AL} in both samples, the Fe^{2+}_{AL} amount which we should observe in the annealed ^{57}Ni-labelled compound can be estimated by:

$$y_{theor} = 0.17\,m + (0.45 + 0.17)\,n,$$

which results in $y_{theor} = 0.28$. This value is to be compared with the experimental value of 30%, which is quite satisfactory.

The assignment of the ferric component to Fe^{3+}_{N} or Fe^{3+}_{AL} can be achieved in the same way. Defining z, z_1 and z_2 as total Fe^{3+}, Fe^{3+}_{N} and Fe^{3+}_{AL} fractions respectively, the Fe^{3+}_{N} amount is given by:

$$z_1 = 0.33\,m = 0.25,$$

and consequently, $z_2 = z - z_1 = 0.11$, represents the total Fe^{3+}_{AL} ($Fe^{3+}_{AL(I)} + Fe^{3+}_{AL(II)}$).

(6) The final comparison between the distributions of the primary nucleogenic species $^{57}Fe^{n+}$ and $^{57}Co^{n+}$ resulting, respectively, from the ^{57}Co and ^{57}Ni decays in $NiC_2O_4\cdot 2H_2O$ gives:

$$^{57}Ni:Ni^{2+} \rightarrow 0.75\,Co^{2+} + 0.25\,Co^{3+}$$

and

$$^{57}Co:Ni^{2+} \rightarrow 0.50\,Fe^{2+} + 0.50Fe^{3+}\ [8].$$

This means that the stabilization in the same charge state as the parent atom is more important in the $^{57}Ni \rightarrow {}^{57}Co$ decay than in the next one. This observation can be explained by several features, such as:

(i) the difference between the redox potentials of Co^{3+}/Co^{2+} and Fe^{3+}/Fe^{2+} couples,

(ii) the difference between the decay schemes of both transitions, with 60% electron capture only in $^{57}Ni \rightarrow {}^{57}Co$, against 100% in $^{57}Co \rightarrow {}^{57}Fe$, and

(iii) the smaller difference between the ionic radii of Co^{2+} (88.5 pm) and Ni^{2+} (83 pm) than between those of Fe^{2+} (92 pm) and Ni^{2+}.

4. SUMMARY AND CONCLUSIONS

The present ^{57}Fe Mössbauer investigation in $^{57}Ni:NiC_2O_4\cdot 2H_2O$ has shown the presence of highly perturbed nucleogenic states of ^{57}Fe generated from the $^{57}Ni \rightarrow {}^{57}Co \rightarrow {}^{57}Fe$ sequence, when the ^{57}Ni decays at low temperature (77 K). The disappearance of these species after warming to RT, together with the similarity observed between annealed ^{57}Ni-labelled and ^{57}Co-doped samples, lead us to assign the initial perturbed states to recoil species, which have arisen from the highly energetic ^{57}Ni decay. Their amount in the emission spectrum (63%) is entirely compatible with the energetics of ^{57}Ni decay and agrees well with previous works.

The observed distribution of ^{57}Fe nucleogenic states has been interpreted by referring to the self-radiolysis model, here adjusted to account for the cumulative effects of the two successive decays. This refinement allowed one to explain the increasing yield of substitutional Fe^{2+} in a perturbed coordination sphere, with respect to the simple transition case ($^{57}Co \rightarrow {}^{57}Fe$). It also permitted an estimate of the initial distribution of primary nucleogenic ^{57}Co atoms (Co^{2+}/Co^{3+}) resulting from the first decay. The comparison of both distributions, concerning either the ^{57}Ni decay in ^{57}Ni-labelled compounds (75% Co^{2+}/25% Co^{3+}) or the ^{57}Co decay in ^{57}Co-doped compounds (50% Fe^{2+}/50% Fe^{3+}) is in total qualitative agreement with comparative nuclear (percentage of electron capture in the nuclear decay scheme), thermodynamic (redox potentials) and steric (ionic sizes) parameters.

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