Europium-151 Mössbauer Spectroscopic Studies of After-effects of the Electron-capture Decay of Gadolinium-151 and the β-Decay of Samarium-151

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^{151}Eu Mössbauer spectrometry has been used to study the after-effects of electron-capture decay of ^{151}Gd and β-decay of ^{151}Sm in inorganic and organic lanthanide compounds doped with these nuclides. No charge state other than ^{151}Eu^{III} was observed following nuclear decay in lanthanide oxides and fluorides doped with ^{151}Gd or ^{151}Sm. However, both the bivalent state, ^{151}Eu^{II}, and the tervalent state, ^{151}Eu^{III}, were observed following the electron-capture decay of ^{151}Gd-doped organic lanthanide compounds. The effects of varying temperature, the organic ligand, and the lanthanide matrix element were investigated. The presence of water of crystallisation was not essential for the production and stabilization of ^{151}Eu^{II} in lanthanide oxalates. The presence of a conjugated organic ligand in ^{151}Gd-doped compounds suppressed the formation of ^{151}Eu^{II}.

THE application of Mössbauer spectrometry to the study of chemical effects of nuclear transformations in solids has two important advantages over conventional radiochemical procedures.[1-5] First, the technique allows an *in situ* analysis of the products of the nuclear transformation. Secondly, the chemical state and the nature of the environment of the product atom can be observed *ca.* 10^{-9} to 10^{-6} s after their formation by the nuclear event, and it should therefore be possible to detect the presence of ' short-lived ' species whose lifetimes are of this order.

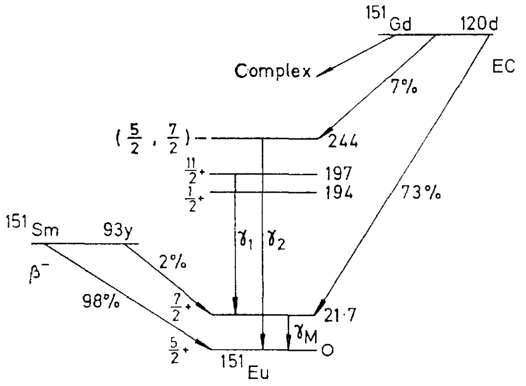

FIGURE 1 Simplified decay schemes of ^{151}Gd and ^{151}Sm leading to the production of ^{151}Eu

Mössbauer studies of after-effects of radioactive decay of lanthanide atoms are of particular interest because the chemical effects normally associated with a change in atomic number are minimised when the radioactive decay occurs between adjacent members of the lanthanide series. The close similarity in chemical properties between the radioactive dopant atoms and the matrix lanthanide atoms will, in most compounds, ensure that the radioactive parent atoms are in a known chemical form.

This paper reports the results of the application of ^{151}Eu Mössbauer spectrometry to the study of the electron-capture decay of ^{151}Gd and, in less detail, of the β-decay of ^{151}Sm. As shown in Figure 1, each of these processes leads to the formation of the Mössbauer nuclide ^{151}Eu. A study of the ^{151}Gd–^{151}Eu electron-capture decay should provide an interesting comparison with the reported studies of the ^{57}Co–^{57}Fe electron capture decay process.[5] Europium can exist in two different oxidation states, Eu^{2+} and Eu^{3+}, which are stable in the solid state and readily distinguishable by means of their isomer shifts. We have investigated the effects of varying both the anion and the lanthanide matrix atoms associated with a radioactive parent atom. We have also attempted to determine the role of water of crystallisation, and the influence of the organic ligand, on the production of aliovalent charge states (that is, in the present case, charge states different from that of the parent atom).

There have been relatively few Mössbauer studies of after-effects reported for lanthanide elements. Probst [6] has reported observing $^{151}Eu^{2+}$ produced by β-decay of $^{151}Sm^{3+}$ incorporated in anhydrous $LaCl_3$. This is an unexpected result since β-decay of $^{151}Sm^{3+}$ in an anhydrous chloride environment would be expected to produce $^{151}Eu^{4+}$ rather than the bivalent state $^{151}Eu^{2+}$. Khurgin, Ofer, and Rakavy [7] have observed the presence of $^{161}Dy^{4+}$ and $^{161}Dy^{3+}$ produced by the β-decay of ^{161}Tb incorporated in CeO_2 and there is somewhat doubtful evidence for the production of $^{153}Eu^{4+}$ following the electron-capture decay of ^{153}Gd incorporated in Gd_2O_3.[8] Mössbauer studies of ytterbium oxide excited by

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[7] B. Khurgin, S. Ofer, and M. Rakavay, *Phys. Letters*, 1970, **33**, *A*, 219.

[8] E. Steichele, W. Henning, S. Hufner, and P. Kienle, in ' Applications of the Mössbauer Effect in Chemistry and Solid State Physics,' I.A.E.A., Vienna, 1966, p. 233.

bombardment with 3 MeV protons failed to produce evidence for radiation-damage effects or for the production of ' anomalous ' charge species.[9]

EXPERIMENTAL

Preparation of ^{151}Gd- *and* ^{151}Sm-*doped Lanthanide Compounds*.—The procedure used for the cyclotron production of ^{151}Gd and the radiochemical techniques used for its isolation have been reported.[10] Approximately 2 mCi quantities of essentially carrier-free ^{151}Gd were prepared as required, and used in the preparation of ^{151}Gd-doped lanthanide compounds.

20 mCi of ^{151}Sm was obtained as Sm_2O_3 (1·16 Ci g^{-1}) from the Radiochemical Centre, Amersham, and used without further purification for the preparation of ^{151}Sm-doped compounds. The 20 mCi ^{151}Sm activity was associated with 17·24 mg of Sm_2O_3, and was not carrier-free.

A number of ^{151}Gd-doped lanthanide complexes were prepared for use as Mössbauer sources by an appropriate scaling down of the methods previously described.[11] In order to obtain Mössbauer sources of suitable activity, 2 mCi of ^{151}Gd was incorporated in *ca.* 20 mg of a lanthanide complex. Although a detailed chemical analysis of the ^{151}Gd-doped lanthanide compounds was not attempted, in every case a sample of the corresponding undoped compound was prepared and analysed. Each ^{151}Gd-doped lanthanide compound was mounted on an aluminium source mount, cooled to the appropriate temperature in a helium-flow cryostat, and its Mössbauer emission spectrum determined. On completion of the Mössbauer emission-spectra studies the compound was removed from the source mount and the ^{151}Gd activity recovered, together with the lanthanide carrier. (Organic ligands, when present, were destroyed by heating the compound to 1200 K.) The lanthanide carrier containing the ^{151}Gd activity was then converted into the next compound to be investigated. In this way a series of compounds of a particular lanthanide carrier with various organic ligands was studied. On completion of such a series of experiments the ^{151}Gd was isolated from the lanthanide carrier by ion-exchange methods, a different lanthanide carrier was added to the ^{151}Gd activity, and a further series of ^{151}Gd-doped compounds prepared and studied. ^{151}Sm-doped lanthanide compounds were prepared, analysed, and mounted in a similar manner to the ^{151}Gd-doped compounds.

The lanthanide compounds which were doped with ^{151}Gd and used as Mössbauer sources in emission spectra studies are listed in the Tables. The organic compounds were selected on the basis of previous studies [11] which showed that they gave characteristic $^{151}Eu^{III}$ absorption spectra observable at room temperature.

Our investigations into the after-effects of ^{151}Sm β-decay have, so far, been limited to ^{151}Sm-doped, $Sm_2(oxalate)_3$,$10H_2O$. It was necessary to use *ca.* 10 mCi of ^{151}Sm in the preparation of ^{151}Sm-doped compounds, since, as shown in Figure 1, the 21·7 keV level of ^{151}Eu is populated by only 2% of the β-decays of ^{151}Sm. For ^{151}Sm of specific activity 1·16 Ci g^{-1} of Sm, the 10 mCi ^{151}Sm activity was necessarily associated with 8·6 mg of Sm_2O_3. Therefore, it was not possible to dope a lanthanide compound with ^{151}Sm without at the same time introducing a significant proportion of samarium into the compound. The emission spectra of ^{151}Gd- and ^{151}Sm-doped compounds were measured within 4 or 5 days of their preparation, and the time taken to measure an emission spectrum was 7 to 10 days. Increasing the storage time to 28 days did not produce an observable effect on the emission spectra.

The Mössbauer Spectrometer.—Mössbauer spectrometer is based on that described by Cranshaw.[12] A Si(Li) diode was employed for detection of 21·7 keV ^{151}Eu γ-ray, and emission spectra of ^{151}Gd- and ^{151}Sm-doped sources were measured relative to a moving room-temperature absorber of isotopically enriched (99·15% ^{151}Eu) $EuF_3,2H_2O$. The ^{151}Gd- and ^{151}Sm-doped sources were mounted in a helium-flow cryostat which allowed emission spectra to be determined with the source at temperatures between room temperature and 4·2 K. The velocity range of the spectrometer was calibrated by means of standard absorbers of $EuSO_4$ and $EuF_3,2H_2O$ and a $^{151}SmF_3,2H_2O$ source. The isomer shift difference between the Eu^{III} and Eu^{II} resonances of these two absorbers was taken to be 14·15 mm s^{-1}.[13]

RESULTS AND DISCUSSION

The emission spectra of ^{151}Gd-doped lanthanide compounds have been investigated with the following objectives in mind: (i) to observe the presence of aliovalent charge states of the ^{151}Eu daughter atoms; (ii) to examine the influence of the ligand, including water of crystallisation, on the production of the aliovalent charge states; (iii) to study the effects of temperature on the emission spectra; and (iv) to compare the after-effects of ^{151}Gd electron-capture decay with those of ^{151}Sm β-decay. In studies of emission spectra the usual roles of source and absorber are transposed, and therefore the sign of the isomer shift will be changed. The isomer shifts reported here are all expressed relative to a $^{151}SmF_3,2H_2O$ standard source at room temperature. Resonances with isomer shifts in the range 0 to −1·2 mm s^{-1} are characteristic of the Eu^{III} charge state and those with isomer shifts in the range +14·4 to +12·0 mm s^{-1} are characteristic of the Eu^{II} charge state.[14]

Two general points should be stressed. First, the percentage resonance absorption of europium resonances observed in an emission spectrum depends not only on the extent of formation of the europium species by the after-effects processes, but also on the recoil-free fractions for emission of the 21·7 keV γ-ray by the ^{151}Eu daughter atoms. In the present work it was not possible to determine the recoil-free fractions of the individual species. Secondly, the velocity range of the transducer

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[12] T. E. Cranshaw, *Nuclear Instr. Methods*, 1964, **30**, 101.

[13] G. Gerth, P. Kienle, K. Luchner, *Phys. Letters*, 1968, **27**, *A*, 557.

[14] N. N. Greenwood and T. C. Gibb, in ' Mössbauer Spectroscopy,' Chapman and Hall, London, 1971, p. 547.

used in this work was +30 to −30 mm s^{-1} and the possibility that resonances of Eu^{I} and Eu^{IV} charge states might be outside the velocity range investigated must be borne in mind. The spectral information was obtained from the Eu^{II} and Eu^{III} resonances by fitting single Lorentzian peaks to the experimental data, since, with a velocity range appropriate to the observation of both resonances in the same spectrum, the experimental data did not reveal sufficient detail of the individual peaks to warrant the application of a quadrupole splitting analysis.

^{151}Gd-*doped Lanthanide Inorganic Compounds.*—The emission spectra of $EuF_3,2H_2O$ and of a number of lanthanide oxides doped with ^{151}Gd were determined (Table 1). In all cases only the expected $^{151}Eu^{III}$ resonance was observed. The absence of any evidence for the formation of $^{151}Eu^{II}$ is in contrast with the production of both $^{57}Fe^{II}$ and $^{57}Fe^{III}$ following the electron-capture decay of ^{57}Co in oxides[15,16] and hydrated fluorides.[17,18]

TABLE 1

Charge states of ^{151}Eu observed following the electron-capture decay of ^{151}Gd-doped inorganic lanthanide compound

^{151}Gd-doped compounds	T/K	Resonances observed [a] $^{151}Eu^{III}$ Absorption (%) [b]	Isomer shift/mm s^{-1}	Width/mm s^{-1}
CeO_2	4·2	5·0 ± 0·1	−0·69 ± 0·04	4·1 ± 0·1
	77	4·6 ± 0·1	−0·89 ± 0·07	4·0 ± 0·2
	295	4·3 ± 0·1	−0·52 ± 0·04	2·7 ± 0·1
Gd_2O_3	4·2	8·5 ± 0·1	−0·97 ± 0·02	3·3 ± 0·1
Tb_4O_7	4·2	3·4 ± 0·1	−1·20 ± 0·10	5·2 ± 0·3
	77	4·5 ± 0·1	−0·93 ± 0·08	3·9 ± 0·2
	295	3·2 ± 0·1	−0·90 ± 0·07	4·3 ± 0·2
Dy_2O_3	4·2	5·0 ± 0·1	−1·17 ± 0·06	4·7 ± 0·1
	77	4·3 ± 0·1	−1·10 ± 0·03	4·2 ± 0·1
	100	3·6 ± 0·1	−1·01 ± 0·03	4·3 ± 0·1
	200	3·6 ± 0·1	−0·90 ± 0·03	3·7 ± 0·1
	295	3·6 ± 0·1	−0·81 ± 0·03	2·9 ± 0·1
Er_2O_3	4·2	8·1 ± 0·1	−1·24 ± 0·02	2·7 ± 0·1
	77	10·8 ± 0·1	−1·30 ± 0·02	3·3 ± 0·1
	295	10·7 ± 0·1	−0·89 ± 0·03	3·4 ± 0·1
$ErF_3,2H_2O$	77	11·7 ± 0·1	−0·97 ± 0·01	3·4 ± 0·1
	295	2·6 ± 0·1	−0·85 ± 0·03	3·9 ± 0·1

[a] No resonance corresponding to charge states other than $^{151}Eu^{III}$ was observed. [b] % Absorption in all the Tables is expressed in terms of the height of an absorption peak as a percentage of the measured baseline.

It is worth noting that we did not observe evidence for the formation of $^{151}Eu^{IV}$ resulting from the electron-capture decay of ^{151}Gd in CeO_2 or Tb_4O_7. This contrasts with the reported identification of $^{161}Dy^{IV}$ following the β-decay of ^{161}Tb in CeO_2 at 4·2 K.[7]

^{151}Gd-*doped Lanthanide Organic Compounds.*—Emission spectra of ^{151}Gd-doped lanthanide organic compounds were investigated with the source at temperatures between 295 and 4·2 K (see Tables 2 and 3).

^{151}Gd-*doped lanthanide oxalates.* The results of our emission spectra studies for a series of ^{151}Gd doped lanthanide oxalates are in Table 2. At and below 77 K all the emission spectra consisted of two resonances which have been unambiguously assigned to $^{151}Eu^{III}$ and $^{151}Eu^{II}$. The emission spectra were little affected by the particular lanthanide element which was used to form the ^{151}Gd-doped oxalate. However, the line-widths of the Eu^{II} resonances appear to increase as the difference in atomic number between ^{151}Gd and the matrix lanthanide increases. This tendency, which is detectable at both 4·2 and 77 K, implies that the degree of variation in the environment of the $^{151}Eu^{II}$ daughter atoms increases with increasing difference in radius between the $^{151}Gd^{3+}$ and the host lanthanide. The percentage absorption of both the $^{151}Eu^{III}$ and $^{151}Eu^{II}$ resonances increased with decrease in temperature. For comparison the percentage absorption was determined as the ratio of the measured peak height to the observed baseline with no background correction. The largest percentage resonant effect for the production of $^{151}Eu^{II}$ daughter atoms was observed for ^{151}Gd-doped $Gd_2(C_2O_4)_3,10H_2O$ at 4·2 K. The spectrum is in Figure 2.

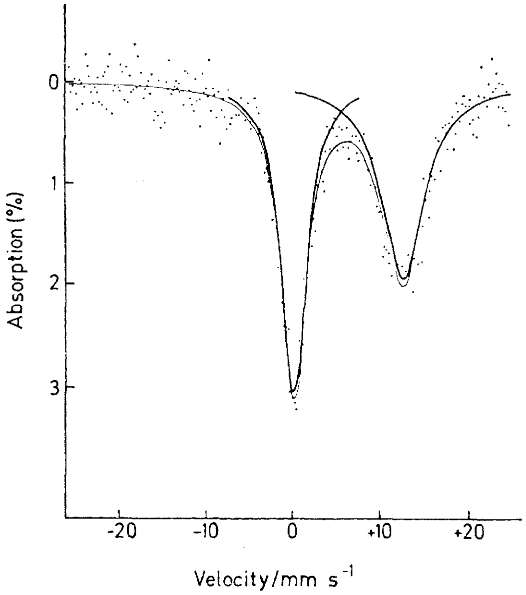

FIGURE 2 Mössbauer spectrum of a ^{151}Gd-doped $Gd_2(C_2O_4)_3,10H_2O$ source at 4·2 K and a $^{151}EuF_3,SH_2O$ absorber at room temperature. The light line represents the fitted spectrum and the heavy lines represent the individual component peaks

In ^{151}Gd-doped lanthanide oxalates the dopant atoms could occupy either normal lattice positions, as $^{151}GdLn(C_2O_4)_3,xH_2O$, or interstitial sites in the $Ln_2(C_2O_4)_3,xH_2O$ matrix, although the former appears more probable. For the case of ^{151}Gd dopant atoms in a $Gd_2(C_2O_4)_3,10H_2O$ matrix we know that essentially all the ^{151}Gd atoms will occupy normal lattice positions. It is likely

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[15] W. Triftshauser and P. P. Craig, *Phys. Rev.*, 1967, **162**, 274.

[16] V. G. Bhide and G. K. Shenoy, *Phys. Rev.*, 1966, **143**, 309.

[17] J. M. Friedt and J. P. Adloff, *Compt. rend.*, 1969, **268**, *C*, 1342.

[18] J. M. Friedt and J. P. Adloff, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 163.

TABLE 2

Charge states of ^{151}Eu observed following the electron-capture decay of ^{151}Gd-doped lanthanide oxalates

		Resonances observed					
		^{151}Eu^{III}			^{151}Eu^{II}		
^{151}Gd-doped compounds	T/K	Absorption (%)	Isomer shift / mm s^{-1}	Width / mm s^{-1}	Absorption (%)	Isomer shift / mm s^{-1}	Width / mm s^{-1}
$La_2(C_2O_4)_3,9H_2O$	4·2	3·1 ± 0·1	−0·39 ± 0·03	3·7 ± 0·1	0·9 ± 0·1	+14·18 ± 0·18	12·6 ± 0·5
	8	3·4 ± 0·1	−0·49 ± 0·04	3·2 ± 0·1	0·9 ± 0·1	+13·71 ± 0·30	12·8 ± 0·8
	77	1·6 ± 0·1	−0·28 ± 0·06	3·8 ± 0·15	0·5 ± 0·1	+14·15 ± 0·39	11·3 ± 1·0
	295		Not observed			Not observed	
$Ce_2(C_2O_4)_3,9H_2O$	4·2	1·5 ± 0·1	−0·63 ± 0·04	8·3 ± 0·2	0·7 ± 0·1	+12·60 ± 0·90	11·6 ± 0·3
	77	1·2 ± 0·1	−0·34 ± 0·17	5·0 ± 0·4	0·3 ± 0·1	+12·10 ± 1·01	10·8 ± 2·0
	295	0·3 ± 0·1	−0·10 ± 0·40	5·2 ± 1·0		Not observed	
$Sm_2(C_2O_4)_310H_2O$	4·2	2·8 ± 0·1	−0·85 ± 0·05	3·6 ± 0·1	1·0 ± 0·1	+13·24 ± 0·22	9·5 ± 0·6
	77	1·8 ± 0·1	−0·56 ± 0·06	3·2 ± 0·2	0·5 ± 0·1	+12·33 ± 0·46	13·0 ± 1·2
	295	0·4 ± 0·1	−0·63 ± 0·16	3·1 ± 0·4		Not observed	
$^{153}Eu_2(C_2O_4)_3,10H_2O$	77	2·1 ± 0·1	−0·42 ± 0·04	3·4 ± 0·1	0·3 ± 0·1	+13·32 ± 0·56	11·7 ± 1·4
	295	0·2 ± 0·1	−0·30 ± 0·19	5·1 ± 0·6		Not observed	
$Gd_2(C_2O_4)_3,10H_2O$	4·2	3·1 ± 0·1	−0·13 ± 0·04	3·7 ± 0·1	2·0 ± 0·1	+13·03 ± 0·07	6·6 ± 0·2
	77	1·2 ± 0·1	−0·10 ± 0·07	3·1 ± 0·2	0·5 ± 0·1	+13·26 ± 0·26	7·2 ± 0·6
	295		Not observed			Not observed	
$Gd_2(C_2O_4)_3$(anhydrous)	4·2	3·2 ± 0·1	−0·52 ± 0·05	3·7 ± 0·1	2·5 ± 0·1	+13·28 ± 0·08	6·3 ± 0·2
$Tb_2(C_2O_4)_3,10H_2O$	4·2	2·4 ± 0·1	−0·64 ± 0·04	3·5 ± 0·1	1·0 ± 0·1	+13·13 ± 0·15	8·9 ± 0·4
	77	1·5 ± 0·1	−0·70 ± 0·08	3·2 ± 0·2	0·6 ± 0·1	+13·56 ± 0·29	6·6 ± 0·7
	295	0·4 ± 0·1	−0·22 ± 0·22	2·4 ± 0·5		Not observed	
$Dy_3(C_2O_4)_3,10H_2O$	4·2	1·7 ± 0·1	−0·72 ± 0·1	5·9 ± 0·1	0·7 ± 0·1	+12·80 ± 0·4	9·9 ± 0·3
	77	1·1 ± 0·1	−0·30 ± 0·1	5·0 ± 0·2	0·7 ± 0·1	+12·84 ± 0·21	7·5 ± 0·5
	295	0·3 ± 0·1	−0·21 ± 0·14	3·3 ± 0·3		Not observed	
$Er_2(C_2O_4)_3,10H_2O$	4·2	3·0 ± 0·1	−0·75 ± 0·03	3·7 ± 0·1	1·3 ± 0·1	+13·37 ± 0·11	9·1 ± 0·3
	20	2·5 ± 0·1	−0·78 ± 0·04	3·6 ± 0·1	1·2 ± 0·1	+13·03 ± 0·14	7·7 ± 0·3
	40	2·5 ± 0·1	−0·63 ± 0·04	3·1 ± 0·1	1·3 ± 0·1	+13·30 ± 0·13	7·3 ± 0·3
	60	1·9 ± 0·1	−0·80 ± 0·06	3·8 ± 0·2	0·9 ± 0·1	+14·04 ± 0·22	8·5 ± 0·5
	77	2·3 ± 0·1	−0·44 ± 0·05	4·0 ± 0·2	0·8 ± 0·1	+13·84 ± 0·20	9·9 ± 0·6
	100	1·9 ± 0·1	−0·50 ± 0·05	2·8 ± 0·2	0·7 ± 0·1	+13·54 ± 0·25	8·1 ± 0·6
	150	1·4 ± 0·1	−0·25 ± 0·09	3·9 ± 0·2	0·5 ± 0·1	+14·05 ± 0·46	11·1 ± 1·2
	200	1·0 ± 0·1	−0·30 ± 0·17	3·1 ± 0·4	0·2 ± 0·1	+13·71 ± 1·50	9·4 ± 3·0
	295	0·9 ± 0·1	−0·34 ± 0·05	4·3 ± 0·2	0·2 ± 0·1	+13·48 ± 0·40	14·4 ± 0·8
$Tm_2(C_2O_4)_3,6H_2O$	4·2	4·0 ± 0·1	−0·51 ± 0·03	3·5 ± 0·1	0·7 ± 0·1	+13·37 ± 0·28	10·9 ± 0·7
	77	2·1 ± 0·1	−0·48 ± 0·06	4·0 ± 0·1	0·4 ± 0·1	+12·60 ± 0·44	12·6 ± 1·2
	295	0·4 ± 0·1	−0·84 ± 0·32	2·4 ± 0·8		Not observed	
$Yb_2(C_2O_4)_3,10H_2O$	4·2	3·4 ± 0·1	−0·68 ± 0·04	3·8 ± 0·1	1·4 ± 0·1	+14·36 ± 0·18	8·7 ± 0·4
	77	2·4 ± 0·1	−0·25 ± 0·05	3·2 ± 0·1	0·6 ± 0·1	+13·83 ± 0·30	7·9 ± 0·7
	295		Not observed			Not observed	
$Lu_2(C_2O_4)_3,6H_2O$	4·2	2·7 ± 0·1	−0·33 ± 0·03	3·6 ± 0·1	0·6 ± 0·1	+13·67 ± 0·25	13·0 ± 0·6
	10	3·5 ± 0·1	−0·39 ± 0·04	3·4 ± 0·1	0·8 ± 0·1	+14·00 ± 0·03	11·2 ± 0·8
	20	2·4 ± 0·1	−0·43 ± 0·04	3·3 ± 0·1	0·5 ± 0·1	+13·81 ± 0·38	9·9 ± 1·0
	77	1·9 ± 0·1	−0·30 ± 0·05	3·7 ± 0·1	0·5 ± 0·1	+13·70 ± 0·33	10·0 ± 0·9
	100	1·7 ± 0·1	−0·43 ± 0·05	3·2 ± 0·1	0·3 ± 0·1	+13·40 ± 0·56	10·0 ± 1·4
	200	0·7 ± 0·1	−0·48 ± 0·14	3·0 ± 0·3	0·2 ± 0·1	+13·78 ± 1·10	11·2 ± 2·8
	295		Not observed			Not observed	

TABLE 3

Charge states of ^{151}Eu observed at 77 K following the electron-capture decay of ^{151}Gd-doped organic lanthanide compounds

	Resonances observed					
	^{151}Eu^{III}			^{151}Eu^{II}		
^{151} Gd doped compounds	Absorption (%)	Isomer shift / mm s^{-1}	Width / mm s^{-1}	Absorption (%)	Isomer shift / mm s^{-1}	Width / mm s^{-1}
H[Ce(dcta)],$4H_2O$	1·4 ± 0·1	−0·60 ± 0·15	4·6 ± 0·4	0·2 ± 0·05	+11·10 ± 2·85	16·5 ± 6·1
H[Er(dcta)],$4H_2O$	2·7 ± 0·1	−0·61 ± 0·02	3·3 ± 0·1	0·3 ± 0·1	+12·56 ± 0·25	8·3 ± 0·6
H[Er(edta)],$3H_2O$	2·7 ± 0·1	−0·50 ± 0·01	3·8 ± 0·1	0·2 ± 0·1	+13·30 ± 0·13	10·1 ± 0·3
Er(Ac·CH·Ac)$_3$,$3H_2O$	3·2 ± 0·1	−0·59 ± 0·02	3·4 ± 0·1	0·4 ± 0·1	+12·20 ± 0·19	6·3 ± 0·3
$Er_2(CH_2{\cdot}C_2O_4)_3,5H_2O$	2·0 ± 0·1	−0·55 ± 0·01	4·3 ± 0·1	0·7 ± 0·1	+13·70 ± 0·05	8·5 ± 0·1
Ce(phen)$_2$Cl$_3$,$2H_2O$	3·4 ± 0·1	−0·58 ± 0·09	3·7 ± 0·2		Not observed	
Dy(phen)$_2$Cl$_3$$2H_2O$	3·4 ± 0·2	−0·52 ± 0·11	3·5 ± 0·3		Not observed	
Ce(tropolonate)$_3$	1·2 ± 0·1	−1·00 ± 0·20	3·4 ± 0·4		Not observed	

edta = ethylenediamine-*NNN'N'*-tetra-acetate; dcta = 1,2-diaminocyclohexane-*NNN'N'*-tetra-acetate; $CH_2{\cdot}C_2O_4$ = malonate; Ac·CH·Ac = acetylacetonate; phen = 1,10-phenanthroline.

that the $^{151}Eu^{II}$ daughter atoms produced by the radiolysis mechanism (see below) will have a greater probability of detection if the ^{151}Gd parent atom initially occupies a normal lattice site.

The line-width of a normal Eu^{II} peak obtained for a europus oxalate monohydrate absorber at 77 K and a $^{151}Gd_2O_3$ source at room temperature is $5{\cdot}1 \pm 0{\cdot}15$ mm s^{-1}.[19] Thus, the line-widths of the $^{151}Eu^{II}$ resonances of the emission spectra are a factor of two greater than the normal absorption peak-widths. This is illustrated in Figure 3 for the $^{151}Eu^{II}$ peak of ^{151}Gd-doped $La_2(C_2O_4)_3,9H_2O$ at 4·2 K, which is broad and asymmetric.

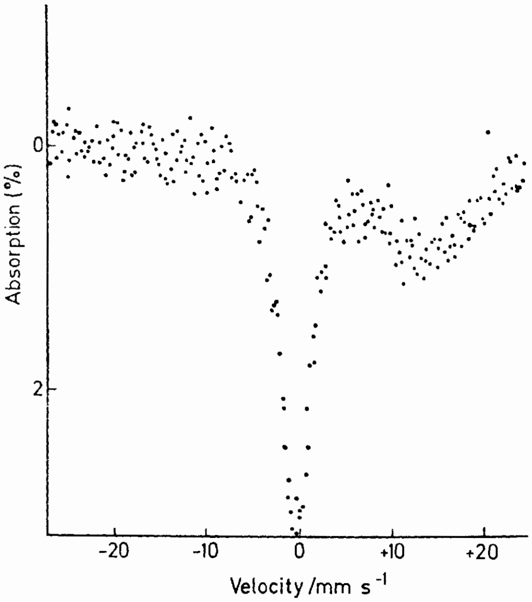

FIGURE 3 Mössbauer spectrum of a ^{151}Gd-doped $La_2(C_2O_4)_3$,$9H_2O$ source at 4·2 K and a $^{151}EuF_3,2H_2O$ absorber at room temperature

Ehnholm *et al.*[20] investigated the absorption spectra of europous oxalate and found that quadrupole splitting could not be detected above 1·9 K for EuC_2O_4, and 2·8 K for EuC_2O_4,H_2O. The large width of the observed $^{151}Eu^{II}$ resonance cannot therefore be explained solely by incipient quadrupole splitting, and it must be concluded that some at least of the $^{151}Eu^{II}$ daughter atoms are not in the normal lattice sites to be expected for Eu^{II} in europous oxalate. Therefore it is likely that the broad $^{151}Eu^{II}$ resonances are due to the stabilisation of $^{151}Eu^{II}$ daughter atoms in a number of different chemical environments before the emission of the 21·7 keV γ-ray. This non-uniformity of the chemical environment in the immediate vicinity of the ^{151}Eu daughter atoms is due to the random nature of the radiolysis initiated by electron-capture decay.

The role of water of crystallisation in the after-effects processes has been examined. Table 2 shows a close similarity between the emission spectra of ^{151}Gd-doped $Gd_2(C_2O_4)_3,10H_2O$ and anhydrous $Gd_2(C_2O_4)_3$. Therefore, for the conditions examined, water of crystallisation appears to exert little influence on the fate of the ^{151}Eu daughter atoms. This contrasts with the findings of Friedt and Asch[21] for ^{57}Co-doped cobalt oxalates.

The formation of $^{151}Eu^{II}$ and $^{151}Eu^{III}$ following electron-capture decay of ^{151}Gd in lanthanide oxalates can be explained as follows. A high positive charge on the daughter atoms results from the Auger cascade which follows the electron-capture process and this charge is very rapidly transferred to the whole molecule. The movement of electrons leads to excitation of the ligand groups, and in some cases the parent molecule may suffer a coulombic explosion as a result of repulsion between the distributed positive charges. Moreover radiolysis of the parent or surrounding molecules may be produced by the Auger electrons. All these processes are complete in *ca.* 10^{-12} s and lead to the formation of radiolysis products, in particular the radical ion $C_2O_4^{-\bullet}$. It has been suggested[22] that the radical ion $C_2O_4^{-\bullet}$ is a reactive reducing species capable of reducing many metals to lower valence states [reaction (1)]. We therefore assume

$$M^{n+} + C_2O_4^{-\bullet} \longrightarrow M^{(n-1)+} + 2CO_2 \qquad (1)$$

that the $C_2O_4^{-\bullet}$ radical ion will, in some proportion of events, bring about reduction of $^{151}Eu^{III}$ daughter atoms to $^{151}Eu^{II}$ before the 21·7 keV γ-ray is emitted.

The widths and isomer shifts of the $^{151}Eu^{III}$ resonances are consistent with the view that the $^{151}Eu^{III}$ daughter atoms are present in a normal oxalate lattice. However, the low sensitivity of the isomer shift of the $^{151}Eu^{III}$ resonance to its chemical environment makes this a tentative assumption. It is therefore not profitable to speculate on the mechanism which might be responsible for returning $^{151}Eu^{III}$ daughter atoms to a normal oxalate lattice environment.

We are unable to estimate what fraction of the $^{151}Eu^{III}$ and $^{151}Eu^{II}$ daughter atoms emit the 21·7 keV γ-ray in a recoil-free manner. On the basis of the above mechanism it is probable that a significant fraction of the ^{151}Eu daughter atoms are present within localised zones of radiation damage and thus are not detected because the 21·7 keV γ-ray is not emitted recoil-free. It is also probable that the recoil-free fractions are not the same for the $^{151}Eu^{II}$ and the $^{151}Eu^{III}$ daughter atoms.

^{151}Gd-*doped lanthanide multidentate complexes.* The emission spectra data for a number of ^{151}Gd doped complexes of cerium, erbium, and dysprosium, with multidentate organic ligands are in Table 3. The ^{151}Gd-doped cerium and erbium complexes with the non-conjugated ligands edta, dcta, acetylacetonate, and malonate, all at 77 K, gave emission spectra which consisted of $^{151}Eu^{III}$ and $^{151}Eu^{II}$ resonances and which were similar to the emission spectra obtained with ^{151}Gd-doped oxalates. These results imply that in the non-conjugated ligand complexes investigated, radiolysis

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of the complex has occurred resulting in the production of reducing radicals which then subsequently reduce some of the ^{151}Eu^{III} daughter atoms to ^{151}Eu^{II}.

The ^{151}Gd-doped conjugated ligand complexes Ce(phen)$_2$Cl$_3$,2H$_2$O, Ce(tropolonate)$_3$, and Dy(phen)$_2$Cl$_3$,2H$_2$O gave emission spectra at 77 K which consisted of the ^{151}Eu^{III} resonance only (Table 3). The influence of conjugated ligands on the aliovalent charge states of ^{57}Fe produced by electron-capture decay of ^{57}Co has been investigated by Nath *et al.*[2,23] The mechanism suggested by Nath for the after-effects of the ^{57}Co–^{57}Fe electron-capture decay assumed that the Auger electrons lost by the ^{57}FeM$^+$ daughter atoms were accepted by the π-bonded ligand with little decomposition and very rapidly returned to the ^{57}Fe^{n+} atom, neutralising its high positive charge. The neutralisation of the positive charge on the ^{57}Fe^{n+} daughter atoms must take place very rapidly in order to prevent coulombic disruption of the ligand.

A mechanism similar to that suggested by Nath for the ^{57}Co–^{57}Fe electron-capture decay process may be responsible for the absence of ^{151}Eu^{II} from the emission spectra of ^{151}Gd-doped lanthanide conjugated complexes, but two other factors may also be important. First, it is unlikely that the conjugated ligand will entirely escape radiolysis, but in the conjugated ligand systems reactive radiolysis products may undergo rapid electron-transfer reactions with the undamaged conjugated ligand groups of surrounding molecules before they can react with the ^{151}Eu^{III} daughter atoms. Secondly, ^{151}Eu^{III} is a more difficult species to reduce to the bivalent state than ^{57}Fe^{III}, and it may be that the radiolysis products resulting from damage of the conjugated ligands are not able to donate an electron to ^{151}Eu^{III}.

β-Decay of ^{151}Sm-*doped* Sm$_2$(C$_2$O$_4$)$_3$,10H$_2$O.—The investigation of the after-effects of β-decay of ^{151}Sm was of a preliminary nature, and was confined to an examination of Sm$_2$(C$_2$O$_4$)$_3$,10H$_2$O doped with 10 mCi of ^{151}Sm. The emission spectrum of this source at 77 K consisted of two resonances (Table 4). The resonance with an isomer shift of $-0{\cdot}32$ mm s^{-1} corresponds to ^{151}Eu^{III}. We expect ^{151}Eu^{II} to be observed at $\pm 13{\cdot}0 \pm 1{\cdot}0$ mm s^{-1} and the peak at $+15{\cdot}2$ mm s^{-1} is outside this range. However, Figure 4 shows that the resonance absorption of this peak is low, and there is a greater uncertainty in the isomer shift than is indicated by the computed error. (The apparent precision is a consequence of attempting to fit a single Lorentzian peak to the experimental data.) It therefore seems probable that this resonance is due to ^{151}Eu^{II} daughter atoms. This observation of a small resonance due to ^{151}Eu^{II} species in Sm$_2$(C$_2$O$_4$)$_3$,10H$_2$O sources is in contrast with the results of Probst *et al.*[6] who did not observe such a resonance at temperatures down to 4·2 K.

TABLE 4

Absorption (%)	Isomer shift mm s^{-1}	Width mm s^{-1}
$19{\cdot}5 \pm 0{\cdot}1$	$-0{\cdot}32 \pm 0{\cdot}1$	$3{\cdot}2 \pm 0{\cdot}1$
$0{\cdot}5 \pm 0{\cdot}1$	$+15{\cdot}2 \pm 0{\cdot}5$	$6{\cdot}5 \pm 0{\cdot}1$

The very much smaller ratio of the percentage resonance absorption of ^{151}Eu^{II} to ^{151}Eu^{II} following β-decay of ^{151}Sm, compared with that following electron-capture decay of ^{151}Gd in oxalates, arises from the small degree of radiolysis of the oxalate matrix produced by the β-decay process when compared with the Auger cascade radiolysis produced by electron-capture decay of the parent atom.[24] Within the velocity range investigated, we did not observe any evidence for the ^{151}Eu^{IV} charge state.

Conclusions.—Mössbauer spectrometry can be used to study the after-effects of radioactive decay in solids. Aliovalent charge species have been observed following the electron-capture decay of ^{151}Gd in doped lanthanide oxalates and multidentate ligand complexes, but not in complexes with conjugated ligands, nor in inorganic compounds. Similar species have been observed following the β-decay of ^{151}Sm in doped lanthanide oxalates. The results reported here for the ^{151}Gd electron-capture decay differ in two important respects from published work on the ^{57}Co electron-capture decay process. First, we did not obtain evidence for the production of charge states with a charge greater than the parent atom. Secondly, water of crystallisation did not play a major role in the after-effects mechanism.

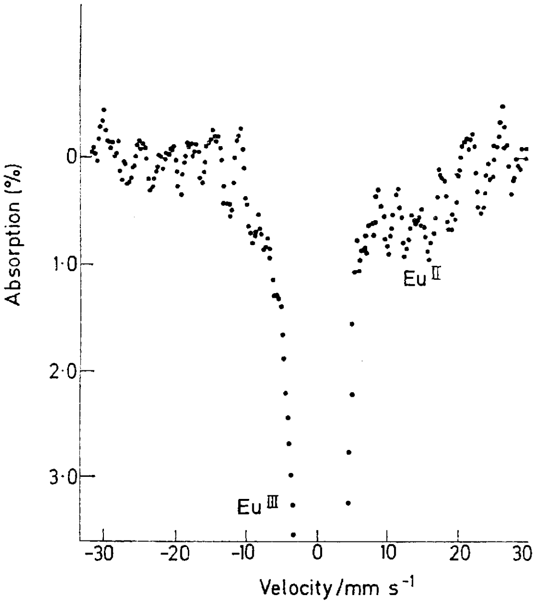

FIGURE 4 Mössbauer spectrum of a ^{151}Sm-doped Sm$_2$(C$_2$O$_4$)$_3$,10H$_2$O source at 77 K and a ^{151} Eu$_2$O$_3$ absorber at room temperature

These results demonstrate the need for caution in extrapolating the results of the ^{57}Co–^{57}Fe after-effects studies to other electron-capture decay processes.

[3/962 *Received*, 14*th May*, 1973]

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