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STUDY OF THE INCORPORATION OF CARRIER-FREE ^{57}Co IN Fe(II) AND Mn(II) OXALATES BY A DOUBLE RADIOACTIVE TRACER METHOD

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The incorporation of carrier-free $^{57}Co^{2+}$ by coprecipitation in Fe and Mn oxalato compounds is characterized by a double radioactive tracer method. This is achieved by labelling the host compound with a short-lived tracer, ^{52}Fe or ^{52}Mn. Activity ratios are measured at several stages, during the precipitation and, afterwards, during the dissolution of the solid. In any case, results indicate very large incorporation yields of ^{57}Co in the precipitate, independently from the intrinsic precipitation yield of the host compound. The observation of a continuous distribution of dopant atoms in the matrix in coprecipitation and dissolution experiments allows to rule out the adsorption of the doping species on a pre-existing precipitate of the host compound and accounts for isomorphous replacement. Incorporation of ^{57}Co in Fe(II) oxalate follows a logarithmic distribution law, giving rise to a concentration gradient of dopant species in the precipitate. Dopant atoms are found to be concentrated in the internal layers of the crystals.

Introduction

The chemical behaviour of atoms at low concentrations has been intensively investigated in relation with widespread use of radioactive tracers in chemistry. Special attention has been drawn to the applicability of separation methods at levels down to 10^5 atoms.[1] As pointed out previously,[2] reliable results are generally expected with procedures in which the atom is submitted many times to the same characteristic step, as in ion exchange chromatography. On the other hand, experiments based on coprecipitation can be considered as "one-step" procedures and are therefore known to give unreliable results and to fail in achieving reproducibility.

The present work has been performed in expectation to an emission Mössbauer study on the after-effects of electron capture decay in some ^{57}Co-doped divalent oxalates, $^{57}Co : M(II)\,C_2O_4 \cdot 2H_2O$ [3] The purpose of the latter study was to detect an eventual matrix effect on the nature and proportions of ^{57}Fe nucleogenic

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species, by comparing the ^{57}Co-labelled Co(II) compound with isomorphous compounds doped with ^{57}Co (M=Mn, Fe, Ni, Zn, Mg). The main question here arises as to whether or not the ^{57}Co doping atom is actually located in a substitutional lattice position, whatever the host cation is. This has to be viewed with respect to the particular incorporation method used, i.e. coprecipitation from a starting solution containing carrier-free $^{57}Co^{2+}$. The Fe(II) and Mn(II) salts have been selected for the present study.

The standard synthesis method

Dihydrated oxalato-compounds are obtained by adding ground oxalic acid in excess to a stirred solution of MCl_2 0.1M heated at 70 °C. X-ray powder diagrams of all the samples are consistent with the monoclinic α-form, isomorphous with oxalite (natural ferrous compound, α-$FeC_2O_4 \cdot 2H_2O$).

When ^{57}Co-doped samples are prepared, carrier-free $^{57}CoCl_2$ is introduced in the solution of the host cation salt, with a specific activity of 3.7 MBq (100 μCi) per millimol of metallic salt, i.e. some $2 \cdot 10^{-5}$% at. This corresponds to about 10^{14} doping atoms per sample millimol. It is worthwhile pointing out that, at such low concentration levels, the thermodynamic precipitation conditions of the pure cobalt compound are never fulfilled.

The double radioactive tracer method

As described above, the main question here concerns the nature of incorporation of ^{57}Co doping species in the matrix. Are they actually located at normal substitutional positions in the host lattice, or are most or some of them adsorbed on a preexisting precipitate of the host compound acting as a substrate?

According to a classification proposed by HAHN,[4,5] four different cases can be encountered when chemically distinct species are coprecipitated from a parent solution: (1) isomorphous replacement, provided the doping and host species have identical crystal structures on a macroscale and in such a way that they are allowed to form isomorphous mixed crystals; (2) anomalous-mixed-crystal formation, when the doping atom enters the host crystal lattice even though macroscopic isomorphism is not observed; (3) adsorption of the doping atom on the surface of the host precipitate; and (4) coprecipitation by "internal adsorption" during the growing of the host crystals.

In the two first cases, i.e. when the doping species enters substitutional lattice sites, the concentration ratio [doping cation/host cation] shows a continuous distribution, which is not necessarily homogeneous, because the dopant species can be concentrated near either the center or the surface of the crystal. On the other hand,

adsorption phenomena can be evidenced by a discontinuous distribution of the doping atoms in the matrix, either on the external surface of the precipitate, or sometimes on internal layers of the crystal.

In the present work, the incorporation of carrier-free $^{57}Co^{2+}$ by coprecipitation in Fe(II) and Mn(II) oxalate has been studied by labelling the host cation with a short-lived radioactive tracer, ^{52}Fe (8.2 h) or ^{52}Mn (5.7 d).

Experimental

The standard synthesis procedure is applied as described above, from a starting solution containing the doping isotope ($^{57}Co^{2+}$) and the host cation tracer ($^{52}Fe^{2+}$ or $^{52}Mn^{2+}$). The corresponding activities, and their ratios, $^{52}Fe/^{57}Co$ or $^{52}Mn/^{57}Co$ are then measured:

(1) in the parent solution, before addition of oxalic acid;

(2) in the supernatant solution, after successive additions of a 0.4M oxalic acid solution and decantation of the precipitate;

(3) in the solid phase, after filtration and drying;

(4) in the successive washing fractions of the precipitate with a constant volume of water.

Countings are performed by γ-ray spectrometry using a Ge(Li)-detector with a useful volume of 80 cm^3, coupled with a Canberra-8603 multichannel analyzer. Peaks at 122, 168 and 744 keV have been selected to determine ^{57}Co, ^{52}Fe and ^{52}Mn activities, respectively.

Results and discussion

Coprecipitation experiments

Incorporation yields. Figures 1 to 5 show the results obtained for the precipitation of ^{57}Co-doped ^{52}Fe-labelled iron oxalate, $^{57}Co : Fe(^{52}Fe)\ C_2O_4 \cdot 2H_2O$. Figure 1 represents the fraction of remaining dopant ^{57}Co (α) and host tracer ^{52}Fe (β) activities observed in the supernatant solution during the precipitation of iron oxalate. Samples have been taken out after successive additions, every five minutes, of 0.5 ml of a 0.4M oxalic acid solution. Initial activities have been normalized to unity. As shown by the experimental curves of Fig. 1, both activities in the parent solution decrease similarly during the precipitation, but slightly faster for the doping species than for the host cation tracer. At the endpoint of the precipitation process, a large proportion of the ^{52}Fe-activity (95%) has been incorporated into the solid phase; as

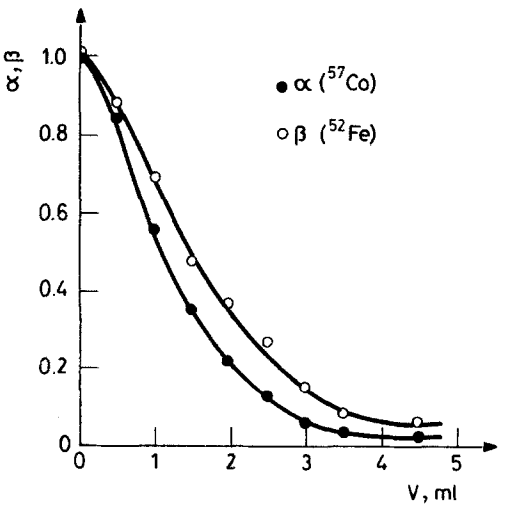

Fig. 1. Precipitation of $FeC_2O_4 \cdot 2H_2O$: fraction of remaining dopant ^{57}Co (α) and host tracer ^{52}Fe (β) activities in the supernatant solution, as a function of volume of added oxalic acid solution

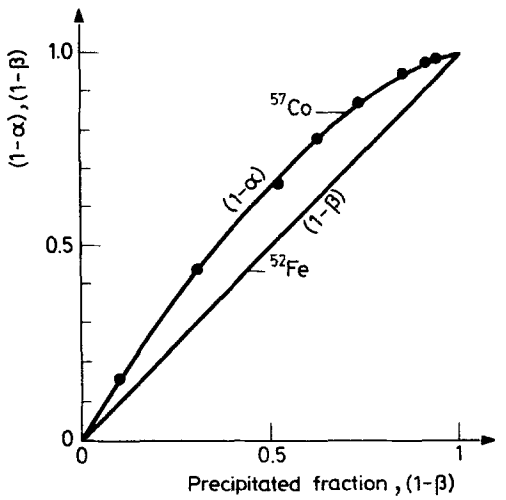

Fig. 2. Precipitation of $FeC_2O_4 \cdot 2H_2O$: activity fractions of ^{57}Co (1-α), and ^{52}Fe (1-β), in the solid phase as a function of the precipitated fraction (1-β)

expected, macroscopic measurements on the collected precipitate indicate a precipitation yield of 95%, which confirms the tracer behaviour of ^{52}Fe. Therefore, the fraction of ^{52}Fe activity which has entered the solid phase, i.e. $(1-\beta)$, has been used as an estimation of the precipitated fraction. By normalizing the precipitation scale in that way, the fraction of ^{57}Co-activity carried in the solid phase, i.e. $(1-\alpha)$ has been plotted against the precipitated fraction $(1-\beta)$, as shown in Fig. 2.

A significant ^{57}Co enrichment is observed in the growing solid phase with respect to the initial solution. The same conclusions can be drawn from a similar coprecipitation study on Mn(II) oxalate. However, in the latter case, the precipitation yield of the host compound is only 45%, which corresponds to the incorporation yield of ^{52}Mn in the precipitate. On the other hand, 97% of the ^{57}Co dopant atoms are incorporated into the manganese compound. Such large incorporation yields of carrier-free $^{57}Co^{2+}$ ions ($\geqslant$97%) have also been observed for all the isomorphous oxalates investigated (M = Fe, Mn, Zn, Mg, Ni), whatever the precipitation yield of the host compound be.

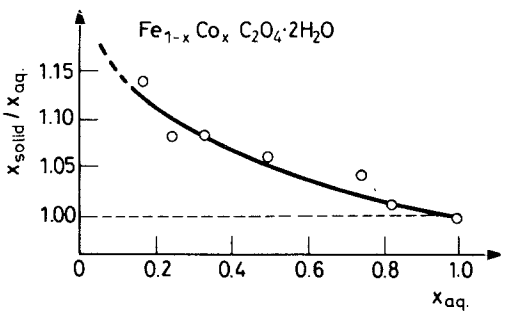

Fig. 3. Precipitation of mixed Fe(II)/Co(II) oxalates: ratio of Co^{2+} contents in solid phase and parent solution as a function of initial Co^{2+} amount in the parent solution

The previous observation can also be compared with the macroscopic behaviour of mixed Fe-Co oxalates, $Fe_{1-x}Co_xC_2O_4 \cdot 2H_2O$, obtained from Fe^{2+}/Co^{2+} parent solutions with low Co^{2+} concentrations. Figure 3 shows the ratio of Co contents in both solid phase and parent solution, as a function of initial Co^{2+} amount introduced in the latter; the difference between Co^{2+} contents in the solid and parent solution increases as the Co^{2+} concentration decreases in the starting solution.

Distribution of the dopant species. As the dopant species (Co^{2+}) and the host cations (Fe^{2+}, Mn^{2+}) presently used give isomorphous oxalato compounds and have similar ionic sizes, they are able to form mixed crystals on a macroscale. Isomorphous replacement can therefore be reasonably expected.

Two different distribution laws are generally invoked to account for isomorphous incorporation of a dopant species in a host precipitate, depending on how the equilibrium is established between doping ions and the solid phase.

If equilibrium is established between ions in the center of the precipitate and those in the surrounding solution, the resulting distribution is homogeneous and follows the Berthelot-Nernst law:

$$\left[\frac{\text{dopant cation}}{\text{host cation}}\right]_{\text{solid}} = D\left[\frac{\text{dopant cation}}{\text{host cation}}\right]_{\text{solution}},$$

where D represents the homogeneous distribution coefficient. D-values greater than unity mean enrichment of the precipitate in dopant species, whereas D-values less than unity indicate enrichment of the solution. Due to slow diffusion rates of ions in crystals at usual temperatures, the establishment of equilibrium between "internal" ions and the solution is often prevented, unless particular experimental conditions are selected to ensure it; this is the case, for instance, when prolonged digestion allows recrystallization to occur. In other cases, however, an instantaneous equilibrium can be reached between the ions in solution and those on the surface of the crystals. This results in a continuous but inhomogeneous distribution of the doping species in the solid phase, the latter being concentrated either near the center, or near the surface of the crystals. This kind of incorporation can be described with a logarithmic distribution law derived by DOERNER and HOSKINS;[6]

$$\ln\left[\frac{\text{total dopant cation}}{\text{dopant cation in solution}}\right] = \lambda \ln\left[\frac{\text{total host cation}}{\text{host cation in solution}}\right]$$

where λ represents the logarithmic distribution coefficient. $\lambda > 1$ means that the precipitate is enriched in dopant species, which are concentrated near the center of the crystals; $\lambda < 1$ indicates enrichment of the solution in dopant species, which are then concentrated near the surface.

For a given precipitation process, the constancy of D or λ indicates the kind of distribution followed. Figure 4 shows the result of such data treatment for the precipitation of ^{57}Co-doped Fe(II) oxalate, where the ^{52}Fe activity has been used as a tracer of the host cation. The constancy of λ argues for the applicability of the Doerner-Hoskins logarithmic distribution law. Submitting the logarithmic data to linear regression (Fig. 5) gives the slope $\lambda = (1.45 \pm 0.03)$. This means, firstly, that the iron(II) oxalate is enriched in ^{57}Co with respect to the solution and, secondly, that the dopant ions are more concentrated at the center of the crystals.

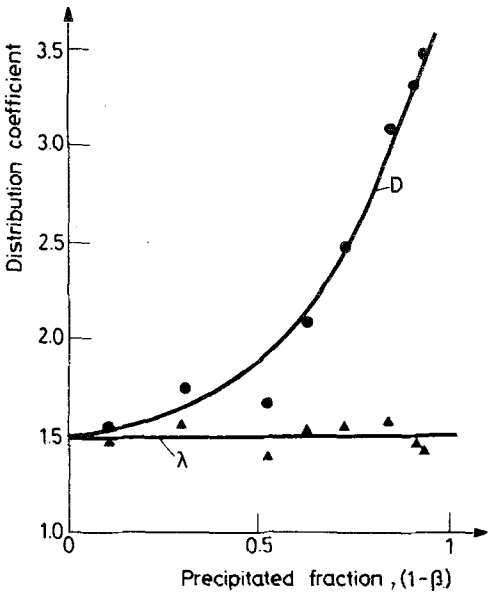

Fig. 4. Precipitation of $FeC_2O_4 \cdot 2H_2O$: distribution coefficients D and λ as a function of the precipitated fraction

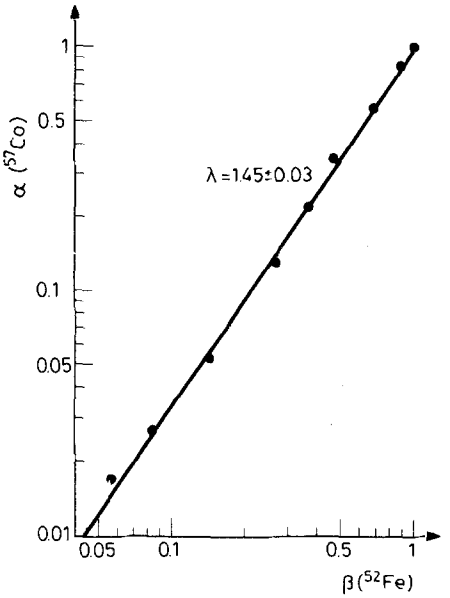

Fig. 5. Doerner-Hoskins bilogarithmic distribution law applied to precipitation of ^{57}Co-doped $FeC_2O_4 \cdot 2H_2O$

Dissolution experiments

The activity ratios of dopant and host cation tracer species observed in the successive leaching fractions, collected when the precipitate has been washed out repeatedly with a constant volume of water, are presented in Figs 6 and 7 for $FeC_2O_4 \cdot 2H_2O$ and $MnC_2O_4 \cdot 2H_2O$, respectively.

Figure 6 is related to the partial dissolution (up to 5%) of Fe(II) oxalate using several fractions of 10 ml water. The evolution observed agrees perfectly well with the conclusions previously drawn from the precipitation experiments. Both continuous distribution of the dopant species and enrichment of it in the internal crystal layers are confirmed by the experimental data, which show an increase of activity ratios $^{57}Co/^{52}Fe$ in the aqueous phase as a function of the dissolved fraction. This experiment shows indeed the existence of a concentration gradient of dopant species towards the center of the crystals, which is in good agreement with Doerner-Hoskins treatment of precipitation data.

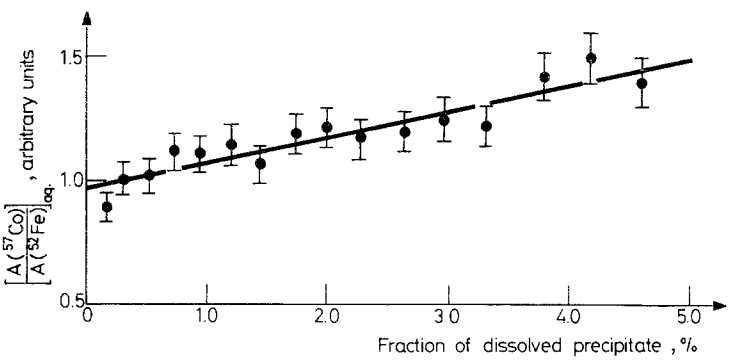

Fig. 6. Ratio of ^{57}Co and ^{52}Fe activities in the washing fractions (10 ml) against dissolved fraction of ^{57}Co-doped ^{52}Fe : $FeC_2O_4 \cdot 2H_2O$

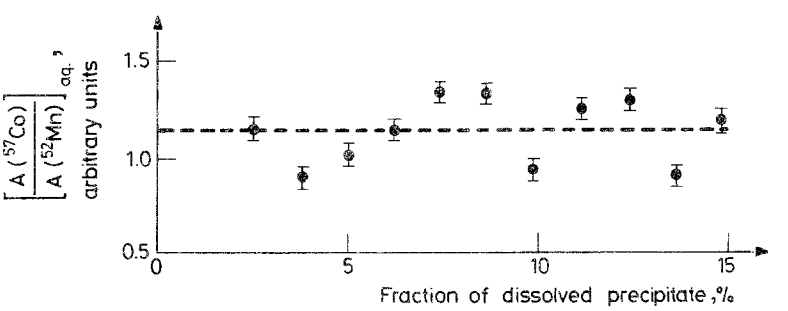

Fig. 7. Ratio of ^{57}Co and ^{52}Mn activities in the washing fractions (20 ml) against dissolved fraction of ^{57}Co-doped ^{52}Mn : $MnC_2O_4 \cdot 2H_2O$

Although the corresponding investigations on Mn(II) oxalate have not been performed so exhaustively, data of Fig. 7 seem to indicate a different behaviour in the case of the manganese compound.

Within the limits of rather dispersed experimental data, activity ratios $^{57}Co/^{52}Mn$ in successive 20 ml leaching fractions are found to be constant over a large range, up to 15% of dissolution. This can be related to a different precipitation mode of Mn(II) oxalate under the present working conditions. After some induction period, the manganese compound has indeed be found to precipitate very fastly, in such a way that an homogeneous distribution can be expected, according to Berthelot-Nernst law. This kind of incorporation could then explain the constancy of $^{57}Co/^{52}Mn$ activity ratios in the aqueous phase.

It is interesting to compare the present observations of a regular incorporation of the dopant species in the crystal with a previous Mössbauer study[7] concerning the adsorption of ^{57}Co and ^{57}Fe on Fe(II) and Co(II) oxalate crystals. Although the corresponding Mössbauer spectra have only poor statistical resolution, they exhibit large variations of the quadrupole splitting ($\Delta \sim 1.30$ to 2.00 mm/s); the corresponding sites have been attributed to ^{57}Co and ^{57}Fe species which are adsorbed inside the solid, but near the surface. Such an effect can result from exchange reactions accompanying the continuous crystallization of $C_2O_4^{2-}$ anions. The same study showed that a prolonged contact between solid and labelled solution allowed to increase significantly the incorporation yield (almost 100% in 30 min), without producing any change of the Mössbauer spectrum. In our cases, absorption and emission Mössbauer spectra of ^{57}Co-doped Fe and Co compounds[3] are found to be consistent with a substitutional replacement of the doping species in the host lattice.

Conclusions

The double radioactive tracer method has allowed to characterize the nature of incorporation of carrier-free $^{57}Co^{2+}$ ions by coprecipitation in Fe(II) and Mn(II) oxalates.

Very large incorporation yields of ^{57}Co have been observed, independently of the intrinsic precipitation yield of the host compound. Precipitation and dissolution experiments indicate a continuous distribution of dopant species in both compounds. The incorporation of ^{57}Co in Fe(II) oxalate is found to follow the Doerner-Hoskins logarithmic distribution law, accounting for an inhomogeneous distribution of dopant species in the host matrix, the dopant being concentrated in the center of the crystals. The existence of ^{57}Co concentration gradient has been confirmed by dissolution experiments.

In both investigated compounds, isomorphous replacement of ^{57}Co in host lattices has been established, excluding any adsorption process on a pre-existing substrate.

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