Dynamics of Fe atoms in Fe-gluconate as seen by Mössbauer spectroscopy

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Received 7 October 2015, revised 21 December 2015
Accepted for publication 8 January 2016
Published 26 February 2016

Abstract

Fe-gluconate was studied by means of the Mössbauer spectroscopy in the temperature interval of 80–305 K. The measured spectra were analyzed in terms of two components (subspectra) and, alternatively, two distributions of the quadrupole splitting. The major component (~85%) was identified as due to high-spin Fe$^{2+}$ ions, while the identification of the minor component (~15%) was not unique: some characteristics are in favor of the high-spin Fe$^{3+}$ state, while other ones are consistent with the low-spin Fe$^{2+}$ state. Values of the Debye temperature were determined for both components from a temperature dependence of the center shift as well as from that of the spectral area, but they are not conclusive as far as the unique identification of the ionic states of Fe in the components is concerned. The force constant for the high-spin ferrous atoms was evaluated to be equal to 44 N m$^{-1}$ (243 cm$^{-1}$).

Keywords: Fe-gluconate, Mössbauer spectroscopy, ferrous iron, ferric iron, Debye temperature, force constant

(Some figures may appear in colour only in the online journal)

1. Introduction

Ferrous gluconate is a metalorganic compound (a salt of gluconic acid) containing iron in its ferrous (Fe(II) or Fe$^{2+}$) form. It has been used in the pharmacological industry for the production of medicaments, e.g. Apo® ferrous, Apotex®, Ascofer®, Fergon®, Ferral®, Simron®, to name just a few, applied in the treatment of iron deficiency anemias. Interestingly, it has also found applications in the metallurgical industry, where it was revealed as an effective inhibitor for a carbon steel [1], and gluconate-based electrolytes were also successfully used to electroplate various metals [2] or alloys [3]. Concerning its medical applications, it is well known that iron intake by humans depends on a number of factors, one of them being its redox state (ferrous or ferric) e.g. [4]. The bioavailability of the ferrous iron lies between 10 and 15% and is 3–4 times higher than the one of the ferric iron e.g. [5]. Consequently, the purity of the iron gluconate is of importance as far as its applications as iron supplementation are concerned. The ferrous iron is known to be prone to oxidation. In fact, Mössbauer effect measurements, which are able to distinguish between different valence states of iron, gave evidence that the ferrous iron constituted less than ~90% of the total iron present in the iron gluconate [6–10], the rest being ferric iron. However, it must be remembered that the detectability of the two forms of iron may be different. In other words the Fe$^{2+}$/Fe$^{3+}$ ratio obtained from the spectral area of the corresponding sub-spectra does not necessarily reflect the real contribution of the two iron phases. In general, as discussed in detail elsewhere [11], for various Fe$^{2+}$- and Fe$^{3+}$-containing oxides, oxyhydroxides, silicates, and carbonates, the so-called f-factor (recoil free fraction), which is responsible for the detectability of a given phase, is higher for ferric iron assuming both types of ions are embedded in the same matrix. The f-related dynamical quantity, namely the Debye temperature, $\theta_D$, can differ by more than 200 K for ferrous and the ferric ions [11]. In other words, the relative amount of the ferric phase derived from the spectral area may be overestimated. For the inorganic compounds mentioned above the overestimation may be as high as 15% for structurally-related compounds [11]. This uncertainty is as high as the amount of the ferric phase in the Fe-gluconate, as determined by Mössbauer spectroscopy [6–10]. The issue of the minor ferric fraction is further
complicated by the fact that the structure of the Fe-gluconate is not precisely known. Neither a recent Mössbauer spectroscopic study with a high resolution spectrometer [12], nor one performed on a high-purity sample by means of five different techniques gave any definite answer on the issue [13]. In Mössbauer spectroscopy, the distinction between the ferrous and the ferric species is based on the values of two spectral parameters: Isomer shift (IS) and quadrupole splitting (QS). Their values depend not only on the valence state but also on the spin state, i.e. low spin (LS) or high spin (HS). As reported elsewhere [14], one cannot uniquely identify the ferric ions, as their IS and QS values overlap with those of Fe$^{2+}$ (LS). In these circumstances, as remarked elsewhere [10], the minor component seen in the Mössbauer spectra commonly regarded as the ferric one may be instead a ferrous low-spin phase. To shed more light on the issue, the present study, aimed at the determination of the Debye temperature, $\theta_D$, of both forms of iron, was undertaken. It is known that the lattice dynamics depends on the crystal symmetry as well as on the charges of vibrating atoms. As mentioned above, the $\theta_D$-values are significantly higher for the ferric phase, which follows from a higher charge of the former, hence a stronger coupling to the lattice. Therefore, it seems of interest to determine the $\theta_D$-values for the two iron components (forms) present in the Fe-gluconate. To the best of our knowledge no such data exist in the available literature.

2. Experimental

2.1. Sample, spectra measurements, and analysis

As a sample Fe-gluconate was used, courtesy of the Chemistry and Pharmacy Cooperative ESPEFA (Krakow, Poland, which uses it for the production of the iron supplement Ascofer®). The $^{57}$Fe-site Mössbauer spectra were recorded in a transmission geometry and within the temperature range of 80–305 K using a standard spectrometer and a sinusoidal drive. The 14.4 keV gamma rays were supplied by a ~20 mCi Co/Rh source. The sample consisting of 200 mg Fe-gluconate in the form of powder was distributed homogeneously on the surface of ~3 cm$^2$, i.e. the density of Fe was ~8 mg cm$^{-2}$. The spectra, examples of which can be seen in figure 1, had the same shape at all the temperatures measured. They were analyzed with two procedures: (A) superposition of two doublets with a Lorentzian shape of lines: One to account for the sub-spectrum associated with ferrous iron (higher intensity and splitting), and the other one (smaller intensity and splitting) to account for the ferric-HS or ferrous-LS phase, and (B) distribution of the quadrupole splitting, QSD. In the latter two distributions of QS with different ISs were assumed. The spectra were successfully fitted with both procedures and the output of the B-procedure is shown in the right-hand panel in figure 1. Here, the peak centered at QS $\approx$ 3 mm s$^{-1}$ corresponds to the ferrous (Fe$^{2+}$-HS) iron, and the one situated at QS $\approx$ 0.8 mm s$^{-1}$ represents the ferric-HS or the ferrous-LS iron. It can be seen that the former has a shoulder on its left-hand side, a feature that indicates the presence of the Fe$^{2+}$ ions experiencing a slightly weaker crystal field. The existence of these ions was also reported previously [6–8, 10], so it seems to be an inherent property of the Fe-gluconate, and its origin remains unknown. It should be also noted that the width of the peak representing the minor component is larger than the one associated with the major component. This may be due to a less ordered structure of the former. Some amorphous features were recently reported to exist in a high-purity Fe-gluconate [13].

Both procedures yielded spectral parameters pertinent to the determination of the Debye temperature, namely a center shift, CS, and the spectral area, $A$, which is related to the recoil free fraction, $f$. These parameters and other ones used in the fitting procedures are displayed in table 1.
3. Results and discussion

3.1. Temperature dependence of the center shift

The temperature dependence of CS can be expressed as follows:

\[
CS(T) = IS(T) + SOD(T)
\]  

Where IS is the isomer shift and SOD is the so-called second order Doppler shift, i.e. a term related to a non-zero mean value of the square velocity of vibrations, \(\langle v^2 \rangle\). Assuming that in the first-order approximation the phonon spectrum can be described by the Debye model, and taking into account that the temperature dependence of IS is weak, so it can be neglected [15, 16], the temperature dependence of CS can be related to the Debye temperature via the second term in equation (1), which reads as follows [16]:

\[
CS(T) = -\frac{3k_BT}{2mc} \left[ \Theta_D^2 \left( \frac{T}{\Theta_D} \right)^3 + \int_0^{\Theta_D} \frac{\Theta_D x^3}{e^x - 1} dx \right]
\]  

(2)

Where \(m\) is the mass of a Fe atom, \(k_B\) is the Boltzmann constant, \(c\) is the speed of light, and \(x = \hbar \omega/kT\) (\(\omega\) being the frequency of vibrations).

The temperature dependence of the average center shift, \(<CS>\), as derived from the two fitting procedures for the major and the minor sub-spectra is presented in figure 2.

It can be seen that the data obtained from the major sub-spectrum hardly depend on the fitting procedure, while the ones derived from the minor spectrum exhibit a high degree of dispersion. To account for the differences in the \(<CS>\) values due to the fitting procedures, the arithmetic average over A and B (indicated in table 2 as C) was calculated, too. The best fit of equation (2) to the three sets of data yielded values of \(\Theta_D\), which are displayed in table 2.

The large errors of the \(\theta_D(CS)\)-values found for the minor component do not permit a conclusion as to whether or not these values are different than those estimated for the major component. In any case they are not significantly higher, as expected for ferric iron [11]. For Ferrum Lek, a commercially available iron-polymaltose complex, in which Fe-bearing ions are ferric, the value of \(\theta_D(CS) = 502(24)\) K was found [17], comparing well with the values expected for ferric iron [11].

3.2. Temperature dependence of the spectral area

Alternatively, the Debye temperature can be determined from a temperature dependence of the recoil-free factor,
The values of the Debye temperature as determined from the temperature dependence of (a) $<\text{CS}>$, $\theta_D$ (CS), and (b) $\ln(\phi/\theta_D)$, $\theta_D$ ($f$) for the major and the minor iron phases.

|          | Major phase (HS-Fe$^{2+}$) | Minor phase |
|----------|-----------------------------|-------------|
|          | A   | B     | C  | A     | B     | C  |
| $\theta_D$(CS) (K) | 438(23) | 460(21) | 445(18) | 367(171) | 315(166) | 357(111) |
| $\theta_D$(f) (K)   | 210(10) | 202(13) | 207(13) | 214(58) | 238(50) | 225(48) |

\[ f = \exp(-k^2 <\chi^2>), \]  
\[ \text{where } k \text{ is the wave vector of the gamma rays and } <\chi^2> \text{ standing for the mean square amplitude of vibrations}. \]  

In the frame of the Debye model the $f$–$\theta_D$ relationship reads as follows [18]:

\[ f = \exp \left[ -\frac{6E_R}{k_0\theta_D} \left( \frac{1}{4} + \left( \frac{T}{\theta_D} \right)^2 \int_0^{\theta_D/T} \frac{x}{e^x - 1} dx \right) \right] \]  

(3)

Where $E_R$ is the recoil kinetic energy, and $k_0$ is the Boltzmann constant.

In a thin absorber approximation $f$ is proportional to a spectral area, $A$, so the latter can be used in a practical application of equation (3) in order to determine $\theta_D$. For this purpose one calculates $\ln(\phi/\theta_D)$ as a function of temperature, where $\phi/\theta_D = A/A_0$, $A_0$ is the spectral area at the lowest temperature measured (in our case 80 K). The values of $\theta_D$ obtained by this method are displayed in table 2. It is clear that they are significantly lower than those derived from the SOD approach. This feature is in line with general findings, e.g. for a metallic iron $\theta_D$(CS) = 421(30) K, while $\theta_D$(f) = 358(18) K [19].

Important, however, is the fact that there is no difference, within the error limit, between the Debye temperature for the major and the minor components, namely, $\theta_D$ = 207(13) K for the former and $\theta_D$ = 225(9) K for the latter, as determined with the f-approach. This is a rather unexpected result, assuming the minor component represents the ferric ions, as the data reported in the literature give clear evidence that the Debye temperature of these ions is significantly higher than the one of the ferrous compounds, e.g. [11]. There are two plausible explanations for the present finding: Either the iron represented by the minor component is in the ferric-HS state, but its crystallographic structure is different (less rigid) than that of Fe atoms present in the major component, or it is in the ferrous-LS state and has the same or similar crystallographic structure as the major component, i.e. the ferrous-HS. In these circumstances regarding the minor form of iron as ferric and suggesting that it is a product of oxidation of the ferrous iron as suggested, e.g. in [9] is very unlikely because this would mean that its structural conditions were the same as those of the ferrous iron. Consequently, the bounding of the ferric ions would be stronger than that of the ferrous ones, hence the Debye temperature of the former should be significantly higher. The present study gives evidence that this is not the case. On the other hand, a recent multi-technique study of the Fe-gluconate revealed some amorphous features in the studied samples of the high-purity Fe-gluconate [13]. If true, one could associate the minor component with the amorphous structure existing within the major crystalline one. The Fe ions present in the former could be ferric but less rigidly bounded than the ones present in the crystalline form of the Fe-gluconate represented in the Mössbauer spectrum by the major component. The values of $\theta_D$ determined in the present study would be in accord with this scenario. Also, the temperature dependence of the spectral areas of the two components, which is evident from table 1, testifies to some differences in the dynamics of Fe-ions present in the two iron ‘phases’ of the Fe-gluconate. Lowering temperature makes the structure of the major ‘phase’ more rigid than the one of the minor ‘phase’.

### 3.3. Energetics of Fe atom vibrations

The knowledge of the SOD and the $f$-factor can be further used to determine average kinetic, $E_K = 0.5m <v^2>$, and potential, $E_P = 0.5D <x^2>$, energies of the vibrations, respectively. $D$ is the force constant, $m$ stands for the mass of an vibration atom, and $c$ for the velocity of light. Taking into account that SOD = $-0.5E <v^2>/c^2$, $E$ being the energy of the gamma rays (14.4 keV in the present case), the average kinetic energy can be expressed as follows:

\[ E_K = -mc^2 \frac{\text{SOD}}{E_\gamma} \]  

(4)
Where \( m \) stands for the mass of vibration atom, and \( c \) for the velocity of light, and \( E_p \) is the energy of the gamma rays (14.4 keV in the present case).

The relationship between \( E_p \) and \( f \) can be, in a similar way, given by the following expression:

\[
E_p = -\frac{1}{2} D \left( \frac{hc}{E_f} \right)^2 \ln f
\]

The absolute values of \( E_K \) can be readily calculated from equation (4), while the absolute values of \( E_p \) cannot as the value \( D \) is here unknown. Concerning the former, an increase in \( E_K \) observed in the temperature interval of 80–305 K is equal to 22.4 meV. In figure 3 the relative changes of the average square velocity, \( <v^2> \), as a function of the average square amplitude of vibrations, \( <x^2> \) are presented. The former were calculated from SOD, and the latter from \( f \). It can be seen they are linearly correlated for the Fe atoms present in both phases. The increase in the two quantities is caused by the increase in temperature (from 80 to 305 K). A tiny anomaly can be seen in the mid-part of the plot in figure 4(a1). The present experiment, however, does not allow a conclusion as to whether it is genuine or an artefact.

The linear \( <v^2> - \Delta <x^2> \) correlation shown in figure 4(a1) can be further used to determine a change of the potential energy, \( \Delta E_p = 0.5D\Delta <x^2> \), due to the increase in temperature from 80 to 305 K. The value one arrives at is 20.6 meV, which remains in fair agreement with the corresponding increase in kinetic energy. It should be added that the thermal energy related to the temperature increase by 225 K amounts to 19.4 meV. It is evident that all three figures are consistent within \( \sim 10\% \).

3.4. Temperature dependence of the quadrupole splitting

The temperature dependence of the QS for the ferrous and the ferric ions was shown to be different [21], as the former QS significantly decreases with \( T \), while for the latter the dependence is weak if any, so it can be used to make a distinction between the two forms of high-spin Fe ions. Figure 5 illustrates the present case. It is clear that the QS \( (T) \) determined from the major doublet (HS-ferrous ions) shows a significant \( T \)-dependence, while QS\( (T) \) obtained from the minor doublet hardly depends on \( T \) as expected for the ferric state. The QS\( (T) \) dependence of the ferrous doublet could be satisfactorily described by the following equation:

\[
QS(T) = QS(T_0) [1 - aT^{3/2}]
\]

It is worth noting that equation (6), whose origin is purely phenomenological and has no sound theoretical explanation, was successfully applied to describe the temperature QS-dependence of several classes of materials including crystalline, amorphous, as well as quasi crystalline alloys, e.g. [22, 23].
4. Conclusions

The results obtained in the present study can be concluded as follows:

(1) Two forms of iron present in Fe-gluconate were detected in the Mössbauer spectra: A major (~85%) component unequivocally identified as containing high-spin ferrous ions, and a minor (~15%) one, whose identification was ambiguous as its spectral parameters (IS and QS) overlap with those characteristic of low-spin ferrous iron.

(2) Debye temperature was determined for both forms using the temperature dependence of (a) the CS and (b) relative spectral area. The former yielded a value of 445(18) K for the high-spin ferrous phase and 357(111) K for the minor component, while the corresponding figures derived from the latter were 207(13) K and 225(48), respectively.

(3) Force constant for bonding of Fe atoms in the high-spin ferrous fraction was calculated to be equal to 44 N m$^{-1}$ or 243 cm$^{-1}$, which is in line with the values characteristic of the HS ferrous ions for other organometallic compounds.

(4) The temperature dependence of the QS of the doublet associated with the high-spin ferrous component follows the $T^{3/2}$ law, while the QS of the minor doublet hardly depends on $T$. The latter feature is typical of high-spin ferric ions.

Acknowledgments

The Ministry of Science and Higher Education of the Polish Government is thanked for their financial support.

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