Lattice Dynamics in Amorphous Fe-Gluconate as Revealed by Mössbauer Spectroscopy

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Abstract

Amorphous Fe-gluconate was studied by means of the X-ray diffraction and Mössbauer spectroscopy. Spectra measured in the temperature range between 78 and 295 K were analysed in terms of three doublets using a thin absorber approximation method. Two of the doublets were associated with the major ferrous phase (~72%) and one with the minor ferric phase (~28%). Based on the obtained results the following quantities characteristic of lattice dynamical properties were determined: Debye temperature from the temperature dependence of the center shift and that of the spectral area (recoil-free factor), force constant, change of the kinetic and potential energies of vibrations. The lattice vibrations of Fe ions present in both ferrous and ferric phases are not perfectly harmonic, yet on average they are. Similarities and differences to the crystalline Fe-gluconate are also reported.

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1. Introduction

Ferrous gluconate, a salt of the gluconic acid, has mainly medical and food additive applications. Concerning the former it is effectively used in the treatment of hypochromic anemia and marked under various trade names such as Ascofer, Fergon, Ferate, Ferralat, FE-40, Gluconal FE and Simron, to list just some of them. Regarding the latter, it is used for coloring foods, e. g. Black olives and beverages and is labelled by the E579 code in Europe. It is worth mentioning that Fe-gluconate was also applied in the metallurgical industry as an effective inhibitor for carbon steel [1], and gluconate-based electrolytes were successfully used to electroplate various metals [2] or alloys [3]. Its chemical formula reads $\text{C}_{12}\text{H}_{22}\text{FeO}_{14}$ (dehydrated) and $\text{C}_{12}\text{H}_{22}\text{FeO}_{14}\cdot2\text{H}_{2}\text{O}$ (hydrated) and iron, whose concentrations lies between 11.8 and 12.5 percent, is present as divalent $\text{Fe}^{2+}$ or Fe(II) – ion which is soluble, hence assimilable by humans. However, a minor fraction (~10-15% relative to the major fraction) of ferric (Fe$^{3+}$) or Fe(III) iron was detected by Mössbauer-effect studies [4-8]. Its origin is unknown and it can be either soluble or insoluble. Clinical studies give evidence that ferric iron medicaments have poorer absorption than the ferrous ones [9], hence they are less effective in the treatment of anemia diseases. The insoluble ferric iron is useless for such treatments, hence its presence in medicaments is undesired. In these circumstances any attempt aimed at the identification of the minor fraction present in the ferrous gluconate is of interest because it can help to get read of it. In a given structure, that can be either crystalline [10] or amorphous [11], the ferric ions should be stronger bounded than the ferrous ones. Consequently, their lattice-dynamical properties, such as the value of the Debye temperature, should be different than those of the ferrous ions. The Mössbauer spectroscopy is known to be relevant technique to study the issue. However, our recent study performed in the temperature range of 80-310K on a crystalline form of the Fe-gluconate did not show any significant difference in the lattice-dynamical behavior of the two types of Fe-ions [12]. In order to shed more light on the issue we have carried out similar measurements on an amorphous form of this compound. The results obtained are presented and discussed in this paper.
2. Experimental

2.1. Sample

The amorphous sample was prepared by dissolving the crystalline specimen in distilled water, then drying it at 50°C in air. The obtained sample’s color was dark green, similarly to amorphous specimen obtained in a different route in ref. [11]. The X-ray diffraction (XRD) studies were carried out using Panalytical Empyrean diffractometer with Cu Kα radiation. For high-temperature XRD studies the Anton Paar HTK 1200 N chamber was used.

Fig. 1 X-ray diffraction studies of Fe-gluconate: a) comparison of crystalline and amorphous (AMO) samples; b) thermal evolution of amorphous sample.
XRD patterns of Fe-gluconate and amorphous specimen are compared in Fig. 1a. It is apparent that in amorphous sample there are no signs of the crystalline order, which is characteristic to the parent compound. The amorphous specimen exhibits a very broad maximum at around 20° deg of 2θ, which corresponds to inter planar distances d ~ 4.6 Å, the additional, much smaller maxima can be noticed at 37° deg of 2θ, which corresponds to half of the aforementioned distance ~ 2.3 Å. The temperature evolution of the amorphous specimen is presented in Fig. 1b. It was evidenced that thermal decomposition in air takes place at temperatures around 150°C, which is similar to the crystalline Fe-gluconate.

2.2. Measurements and Analysis

$^{57}$Fe Mössbauer spectra were recorded in a transmission geometry using a standard spectrometer with a drive working in a constant acceleration mode. A powdered sample with iron concentration of ~10 mg per cm$^2$ was placed in a cryostat and the temperature of measurements was changed between 78 and 295 K using liquid nitrogen as a coolant. The 14.4 keV gamma rays were provided by a $^{57}$Co/Rh source kept at room temperature. Its activity enabled recording a good quality spectrum within a 3 days run. The temperature of the sample was kept constant within ±0.1 K accuracy during each measurement. Examples of two spectra are shown in Fig. 2. They are similar yet not identical to those recorded on the crystalline compound [7,12]. The most visible difference is a higher intensity of a minor component (about 2-fold) and more symmetrical outermost lines.

The spectra were analyzed in terms of three doublets using a thin approximation protocol: two of them viz. D1 and D2, based on their spectral parameters, were associated with Fe$^{2+}$ or Fe(II) ions, and one, D3, with Fe$^{3+}$ or Fe(III) ions. The following spectral parameters were fitted: spectral area (Ak), center shift (CSk), quadrupole splitting (QSk), line width (Gk) where k=1, 2, 3. This analysis yielded statistically very good fits, and the best-fit parameters are displayed in Table 1.
Fig. 2 Examples of two spectra recorded at various temperatures shown. Indicated are three sub spectra D1, D2 and D3 in terms of which the spectra were analyzed.

Table 1

Best-fit spectral parameters obtained by fitting Mössbauer spectra of the amorphous sample of the Fe-gluconate with the thin absorber approximation method. The meaning of the symbols is as follows: $T$ – temperature, $A_k$ – relative spectral area for three components ($k=1,2,3$), $C_{Sk}$ – center shift for the three components, $<CS>$ - average center shift, $Q_{Sk}$ – quadrupole splitting for the three components, $<QS>$ - average quadrupole splitting, $G_k$ – full line width at half maximum for the three components, $a_k$ – quantity proportional to the recoil-free fraction (normalized spectral area for the $k$-th component). Typical errors: $\pm 0.5\%$ for $A_1$ and $A_2$, $\pm 1\%$ for $A_3$; $\pm 0.003$ for $C_{S1}$ and $C_{S2}$ and $\pm 0.008$ for $C_{S3}$; $\pm 0.01$ for $Q_{S1}$ and $Q_{S2}$ and $\pm 0.02$ for $Q_{S3}$; $\pm 0.01$ for $G_1$, $G_2$ and $G_3$. 
3. Results and Discussion

3.1. Debye Temperature

The Debye temperature, \( \Theta_D \), regarded as a measure of the lattice stiffness, can be determined either from a temperature dependence of (1) center shift, \( CS \), or from (2) recoil-free fraction, \( f \). The former can be expressed as follows:

\[
CS(T) = IS(T) + SOD(T)
\]  \( (1) \)

Where \( IS \) stays for the isomer shift and \( SOD \) is the so-called second order Doppler shift i.e. a quantity related to a non-zero mean value of the square velocity of vibrations, \( \langle v^2 \rangle \), hence kinetic energy. Assuming that the phonon spectrum can be described by the Debye model, and taking into account that \( IS \) hardly depends on temperature, hence it can be neglected [13,14], the temperature dependence of \( CS \) can be thus related to \( \Theta_D \) via the second term in eq. (1) that has the following form [14]:

\[
CS(T) = -\frac{3k_B T}{2mc} \left( \frac{3\Theta_D}{8T} \right) + \int_0^{\Theta_D} \frac{x^3}{e^{x^2/2T} - 1} dx
\]  \( (2) \)

Here \( m \) stays for the mass of the Fe atom, \( k_B \) is the Boltzmann constant, \( c \) is the speed of light, and \( x = \hbar \omega / kT \) (\( \omega \) being frequency of vibrations).
An example of a $CS1(T)$ dependence is presented in Fig. 3, and all $\Theta_D$-values obtained for the three components using this approach are displayed in Table 3.

![Graph of CS1(T) dependence](image)

Fig. 3 Temperature dependence of the center shift of the component D1, $CS1$. The solid line represents the best fit of the data to eq. (2).

### Table 2.

Values of the Debye temperature, $\Theta_D$, as determined from the temperature dependence of the center shift, $CS_k$, of particular components ($k=1, 2, 3$), and that of the average center shift, $<CS>$, as well as from the quantity proportional to the recoil-free fraction, $a_k$. For comparison, corresponding values determined for the crystalline sample (Ref. 12) have been added.

| Amorphous sample | CS1* | CS2* | CS3* | $<CS>$* | $a_1$ | $a_2$ | $a_3$ |
|------------------|------|------|------|---------|------|------|------|
| $\Theta_D$[K]    | 377(9)| 231(12)| 672(29)| 276(24)| 204(4)| 209(4)| 241(9)|
| Crystalline sample [12] |
| $\Theta_D$[K]    | 437(21)| 346(149)| 423(40)| 206(12)| 226(52)|

* in mm/s
As can be seen the $\Theta_D$-values are characteristic of the sub spectrum. In particular, $\Theta_D$ determined from the CS1(T) is by ~50% bigger than the one found from the CS2(T). This finding testifies to a heterohenous structure of the major component of the Fe-gluconate. Fe$^{2+}$ ions associated with the D2 component have lower values of $QS$ and very similar $CS$ ones. This means that they occupy positions with a slightly higher or less deformed symmetry than those associated with the D1 sub spectrum.

Significantly higher value was determined from the CS3(T) dependence, hence depicting the Fe$^{3+}$ ions. This can have two reasons: (1) stronger binding of Fe$^{3+}$ ions due to their larger charge and/or (2) different crystallographic structure of the minor component of the studied compound. $\Theta_D$ can be alternatively figured out from a temperature dependence of the recoil-free fraction, $f=\exp(-k^2<x^2>)$, $k$ being the wave vector of the gamma rays and $<x^2>$ stands for the mean square amplitude of vibrations. In the frame of the Debye model the $f-\Theta_D$ relationship reads as follows [15]:

$$f = \exp \left[ \frac{-6E_R}{k_B\Theta_D} \left( \frac{1}{4} + \left( \frac{T}{\Theta_D} \right)^2 \int_0^{x_D} \frac{xdx}{e^x - 1} \right) \right]$$

(3)

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

In the thin absorber approximation $f$ is proportional to a spectral area, $A$, so the latter is used in a practical application of eq.(3) in order to determine $\Theta_D$. However, the value of the spectral area for a given sample and measurements conditions depends on the number of counts. In order to take this into account, we considered a normalized value of $A_k$, $a_k=(A_k/B_k)/a_k(78K)$, where $B_k$ stays for the number of counts in background of a given spectrum.
Fig. 4 Temperature dependence of $\ln(a_1)$. The solid line stays for the best-fit of the data to eq. (3).

The values of $\Theta_D$ achieved from this spectral parameter for the three components are also displayed in Table 2. Their values are smaller than those found from the CS(T) dependences, yet the $\Theta_D$-value associated with the D3-component is greater than the ones related to D1 and D2 doublets. It is of interest to compare these results with the ones received for a crystalline sample of the Fe-gluconate [12]. Noteworthy, the $\Theta_D$-values derived from the spectral area are practically the same and equal to ~200 K. However, the values acquired from CS(T) are different. Whereas for the crystalline sample they had, within experimental error, similar values (~400 K), for the amorphous sample $\Theta_D$ for the minor phase (Fe$^{3+}$) is by a factor 2-3 larger. In addition, the two components, into which was analyzed the major phase (Fe$^{2+}$) of the amorphous sample, have significantly different values of $\Theta_D$, while this was not so in
the case of the crystalline sample. This relationship has been reflected in the values of $\Theta_D$ derived from the temperature dependence of the average center shift, $\langle \text{CS}\rangle(T)$. 

3. 2. Energetics of Vibrations  

It is of interest to express the vibrations of Fe atoms associated with the three components in terms of the underlying kinetic, $E_K$, and potential, $E_P$, energies. The average kinetic, $E_K=0.5m<\nu^2>$, and potential, $E_P=0.5F<x^2>$ (in harmonic approximation) energies of the lattice vibrations can be determined assuming the SOD and the $\hbar$-factor are known. The force constant is denoted by $F$, $m$ is the mass of an vibrating atom (here $^{57}$Fe) and $c$ is the velocity of light. Taking into account that by definition $SOD=-0.5E_{\gamma}<\nu^2>/c^2$, $E_{\gamma}$ being the energy of the gamma-rays (14.4 keV in the present case), the average kinetic energy can be expressed as follows:

$$E_K = -mc^2 \frac{SOD}{E_{\gamma}} \quad (4)$$

The relationship between $E_P$ and $\hbar$ is, in turn, given by the following term:

$$E_P = -\frac{1}{2}F \left( \frac{\hbar c}{E_{\gamma}} \right)^2 \ln f \quad (5)$$

$E_K$ can be readily calculated from eq. (4) using the SOD-values measured in the Mössbauer experiment, whereas $E_P$ cannot as the value of $F$ has also to be known. Concerning the former the calculated changes of $E_k$ based on formula (4) are plotted vs. temperature in Fig. 5.
Fig. 5 Change of the kinetic energy, $\Delta E_k = E_k(T) - E_k(78K)$, vs. temperature, $T$, for the three components D1, D2 and D3.

It is worth to observe that the change of the kinetic energy, $\Delta E_k = E_k(T) - E_k(78K)$, significantly depends on the component, being the largest for D2 and the smallest for D3. This gives a strong evidence that the kinetic energy of the lattice vibrations (1) in the ferric phase are unquestionably different than those in the ferrous phase and (2) the ferrous phase is heterogeneous as far as the kinetic energy of lattice vibrations are concerned. Noteworthy, the average change of the kinetic energy, $<\Delta E_k> = 20.1$ meV, agrees quite well with the change due to the increase of temperature, $\Delta E = k_B \Delta T = 18.7$ meV what supports our present calculations depicting the energy of vibrations.

Before we will discuss the issue more deeply, it is reasonable to first determine corresponding changes in $E_p$. To this end, as already mentioned, the knowledge of $F$...
is necessary. As shown elsewhere [12], this knowledge can be obtained based on a linear correlation between a change of $\langle v^2 \rangle$, $\Delta \langle v^2 \rangle = \langle v^2 \rangle(T) - \langle v^2 \rangle(78K)$, and that of $\langle x^2 \rangle$, $\Delta \langle x^2 \rangle = \langle x^2 \rangle(T) - \langle x^2 \rangle(78K)$. Figure 5 displays such correlations for D1, D2 and D3.
Fig. 6 Relationships between $\Delta <v^2>$ and $\Delta <x^2>$ for the three sub spectra D1, D2 and D3. The data were fitted to a linear equation. The best fits are marked by linear lines.

The value of $F_k = m \cdot \alpha_k$, where $\alpha_k$ stays for the slope of the line for the $D_k$ component. In this way the following values of the force constant were obtained: $F_1 = 50.8$ N/m, $F_2 = 69.4$ N/m and $F_3 = 43.6$ N/m. As can be seen they are characteristic of the sub spectrum. Interestingly, the value of $F$ as determined for the ferrous Fe-ions in the crystalline sample was equal to 44 N/m [12], hence significantly less than $F_1$ and $F_2$ in the present case. Knowing the $F_k$-values and using the formula (5) we have calculated relative changes of $E_p$, $\Delta E_p(T) = E_p(T) - E_p(78K)$, for D1, D2 and D3. Figure 7 illustrates the obtained results.
Fig. 7 Change of the potential energy, $\Delta E_p = E_p(T) - E_p(78K)$, vs. temperature, $T$, for the three components D1, D2 and D3.

Here the differences between the three components are small, especially at lower temperatures. In the case of harmonic oscillations the changes of the two forms of the mechanical energy should be exactly the same. In order to see whether or not this is the case here, we have plotted a relationship between $\Delta E_k$ and $\Delta E_p$ for each component. The results obtained are displayed in Fig.8.
Fig. 8 Relationship between $\Delta E_k$ and $\Delta E_p$ for the three sub spectra D1, D2 and D3. The lines represent the best linear fits to the data.

It follows from Fig. 8 that in each case the slope is different than 1 what means that the vibrations of Fe ions are not strictly harmonic. The least deviation from the harmonicity is found for the D1 sub spectrum and the highest deviation is observed for the D2 component. This difference shows again that the ferrous phase is heterogeneous. The Fe ions in the ferric phase also exhibit 30% deviation from the harmonic mode, but here the slope is < 1 what means that the change in the potential energy is larger than the one in the kinetic energy. However, the maximum value of the potential energy change, $\langle E_p \rangle=20.4$ meV, what perfectly agrees with the corresponding change of the kinetic energy, $\langle E_k \rangle=20.1$ meV. This means that, on average, the vibrations of Fe-ions present in the studied sample are harmonic.

Concerning the Ferrous ions, at least two components, D1 and D2, can be distinguished that not only have small, yet measurable, differences in spectral parameters, but they also differ in the values of the Debye temperature, kinetic energy of vibrations as well as the spring constants. Due to a smaller values of $QS2$
than those of \( QS1 \) we can assume that the environment of \( Fe^{2+} \) ions associated with D2 has slightly higher symmetry or less deformed environment. Perhaps the investigated Fe-gluconate exists in form of small particles and the D2 component is associated with \( Fe^{2+} \) occupying particles’ core while the D1 one with those ferrous ions that are located on the particles’ surface or close to it.

### 3.3. Quadrupole Splitting

It was reported that a temperature dependence of the quadrupole splitting for the ferrous and the ferric ions was different [16]. For 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. It is thus of interest to verify whether or not this observation is valid in the present case. The temperature dependence of the quadrupole splitting, \( QS(T) \), can be satisfactorily described by the following phenomenological equation [17,18]:

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

(4)

Figure 9 gives evidence that also presently found \( QS(T) \) – values can be very well described by this equation.

The \( T \)-dependence of \( QS3 \) i.e. the one associated with the ferric (\( Fe^{3+} \)) phase is in fact significantly weaker that the corresponding dependences found for the ferrous (\( Fe^{2+} \)) components. This finding can be regarded as a strong argument that the Fe-ions associated with the minor phase are trivalent.
Fig. 9 Temperature dependences of $Q_{Sk}(T)$ for the three sub spectra ($k= 1, 2, 3$). Solid lines represent the best fits of the data to eq. (4).

4. Conclusions

The presently found results on the amorphous Fe-gluconate permit drawing the following conclusions:

1. Iron is present in form of Fe$^{2+}$ ions ($\sim$72%) and Fe$^{3+}$ ones ($\sim$28%).

2. The major phase (ferrous) is not homogenous and it can be decomposed, at least, into two equally-shared components having different values of the quadrupole splitting, Debye temperature, force constant, and kinetic energy of vibrations.

3. Ferric ions have significantly different lattice dynamical properties than the ferrous ions: much higher value of the Debye temperature determined from the center shift, lower value of the force constant as well as that of the kinetic energy of vibrations.

4. Vibrations of Fe ions associated with the three components deviate slightly from the harmonic ones, yet on average the vibrations are harmonic.

5. Temperature dependence of $QS_3$ is much weaker than that of $QS_1$ and $QS_2$. 
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