

# Anomalous Mössbauer line broadening for nanosized hydrous ferric oxide cores in ferritin and its pharmaceutical analogue Ferrum Lek in the temperature range 295–90 K

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**Abstract** Mössbauer spectra of ferritin and its pharmaceutical analogue Ferrum Lek, both containing nanosized hydrous ferric oxides cores in the forms of ferrihydrite and akaganéite, respectively, were measured in the temperature range 295–90 K. An anomalous line broadening with temperature decrease was observed for ferritin below  $\sim 150$  K and for Ferrum Lek below  $\sim 130$  K. Some anomalies were also observed below these temperatures for spectral area and quadrupole splitting.

**Keywords** Nanosized hydrous ferric oxides cores · Mössbauer spectroscopy · Anomalous line broadening · Ferritin · Ferrum Lek

## Introduction

Iron storage protein ferritin contains nanosized mineral hydrous ferric oxide core in the form of ferrihydrite ( $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$ ) with varying degrees of crystallinity and the presence of some inorganic phosphates (Harrison and Arosio 1996). This core contains up to 4,500 iron atoms, and the core size may vary from  $\sim 4$  till  $\sim 8$  nm. Details about ferritin and its iron core structure can be found in Harrison and Arosio (1996), Aisen and Listowsky (1980) and Theil (1987). One of the commercial pharmaceutical analogues of ferritin produced by Lek, Slovenia is Ferrum Lek which is used for treatment of iron deficiency. Ferrum Lek also contains nanosized mineral hydrous ferric oxide core in the form of akaganéite ( $\beta\text{-FeOOH}$ ). The size of this core is about 8 nm. Both iron cores are surrounded with a shell: 24 protein subunits in ferritin and polymaltose in Ferrum Lek.

Mössbauer spectroscopy is an efficient technique to study various iron containing species, and has been widely applied for the study of nanosized hydrous ferric oxide cores in various ferritins and its pharmaceutical analogues such as Imferon, Maltofer<sup>®</sup>, Ferrum Lek, etc. (see, for instance, Kilcoyne and Gorisek

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1998; Bonville and Gilles 2001; Funk et al. 2001; Oshtrakh et al. 2001; 2008; 2011; Chua-anusorn et al. 2002; Bauminger and Harrison 2003; Madsen et al. 2008; Papaefthymiou 2009, 2010).  $^{57}\text{Fe}$  Mössbauer spectra of nanosized hydrous ferric oxide cores in these systems at the temperatures above 80 K are mainly doublets reflecting superparamagnetic state. Mössbauer spectra demonstrate appearance of magnetic sextets in addition to doublet when the rate of superparamagnetic relaxation decreases below the critical rate at the blocking temperature which depends on the particle size (Mørup et al. 1980). The low-temperature region (below 80 K) was studied in detail (for review see Papaefthymiou 2010). In order to elucidate the differences between the iron core structure in ferritin and Ferrum Lek, we studied nanosized hydrous ferric oxide cores in human liver ferritin as a natural product and in commercial pharmaceutical product Ferrum Lek using  $^{57}\text{Fe}$  Mössbauer spectroscopy in the temperature range 295–20 K.

## Materials and methods

Normal human liver ferritin was prepared in lyophilized form at the Russian State Medical University, Moscow, Russian Federation (method of ferritin preparation was briefly described by Oshtrakh et al. 2001 and in references therein). Purified ferritin (more than 95 %) contained about 20 % of bound iron. Powdered sample of 100 mg of protein was packed into the Plexiglas sample holder. Commercial pharmaceutical product Ferrum Lek (Lek, Slovenia) in the form of tablets was used as ferritin analogue. Each Ferrum Lek tablet contained 100 mg of Fe. Sample was prepared from one third of the tablet by powdering and was packed into the sample holder. The sample thickness of Ferrum Lek powder did not exceed 10 mg  $\text{Fe}/\text{cm}^2$ .

$^{57}\text{Fe}$  Mössbauer spectra were measured using an automated precision Mössbauer spectrometric system built on the base of the SM-2201 spectrometer with a saw-tooth shape velocity reference signal formed using 4096 steps of digital–analog convertor and temperature variable liquid nitrogen cryostat with moving absorber. Details and characteristics of this spectrometer are given by Oshtrakh et al. (2009), Semionkin et al. (2010) and Oshtrakh and Semionkin

(2013). The  $^{57}\text{Co}(\text{Rh})$  source of  $\sim 1.0 \times 10^9$  Bq was used at room temperature. Spectra were measured in the temperature range between 295 and 90 K in transmission geometry and registered in 4096 channels. Statistical counts for ferritin were in the range of  $8.3 \times 10^5$ – $2.0 \times 10^6$  counts per channel and the signal-to-noise ratios were in the range of 51–100, and those for Ferrum Lek samples were in the range of  $2.6 \times 10^5$ – $6.3 \times 10^5$  counts per channel and the signal-to-noise ratios were in the range from 101 to 141. Mössbauer spectrum of Ferrum Lek sample was also measured at 90 K in a large velocity range using mentioned Mössbauer spectrometric system. Additionally, measurements of the spectra of Ferrum Lek sample at 80, 70, 60, 40 and 20 K and ferritin sample at 80, 70, 60 and 20 K were carried out using a KFKI type spectrometer with a low velocity resolution (triangular velocity reference signal formed using 512 steps of digital–analog convertor for both direct and reverse motion) and APD close cycle refrigerator. Mössbauer spectra at 80, 70 and 60 K were measured using a small velocity range, while those at 40 and 20 K were measured in a large velocity range. The low velocity resolution spectra were registered in 250 channels on the direct and reverse motion and folded.

In order to emphasize changes reflected by our measurements as a function of temperature, first we characterize the observed spectra in a model-independent way, by deriving their relative absorption area, the first moment and the second central moment as follows. The  $b$  baseline that equals to the expected value of counts far enough from resonance can be readily estimated in the case of the present spectra by fitting them to a number of Lorentzians that provides a statistically acceptable fit. Once this is accomplished, the spectra can be normalized as

$$y_i = \begin{cases} \frac{b-n_i}{b} & \text{if } n_i \leq b \\ 0 & \text{if } n_i > b \end{cases},$$

where  $n_i$  denotes the measured counts in the  $i$ th channel. The  $y_i$  values thus observed are further normalized to give a sum of unity as

$$p_i = \frac{y_i}{\sum_i y_i}.$$

The  $p_i$  values can be treated as a probability distribution over the channels, and as such can be meaningfully characterized by the first moment

(mean,  $m$ , central shift) and the second central moment (variance) or the square root of the latter (standard deviation,  $\sigma$ ). Accordingly, we calculate the corresponding quantities as

$$m_{\text{ch}} = \sum_i i p_i,$$

$$\sigma_{\text{ch}} = \sqrt{\sum_i (i - m_{\text{ch}})^2 p_i},$$

where the index “ch” indicates that the quantities are expressed in channels. Finally, we convert these quantities to the corresponding velocity values  $m$  and  $\sigma$  via

$$m = \Delta v \cdot (U p m_{\text{ch}} - n_0),$$

$$\sigma = \Delta v \cdot \sigma_{\text{ch}},$$

where  $\Delta v$  and  $n_0$  denote the calibration factor and the zero velocity channel, respectively. With the above notation, the relative absorption area  $a$  can be given as

$$a = \Delta v \cdot \sum_i \frac{b - n_i}{b}.$$

Changes in the quantities  $m$ ,  $\sigma$  and  $a$  are expected to reflect corresponding changes in the physical quantities of the  $^{57}\text{Fe}$  isomer shift, line width and quadrupole splitting, and the recoilless fraction, respectively.

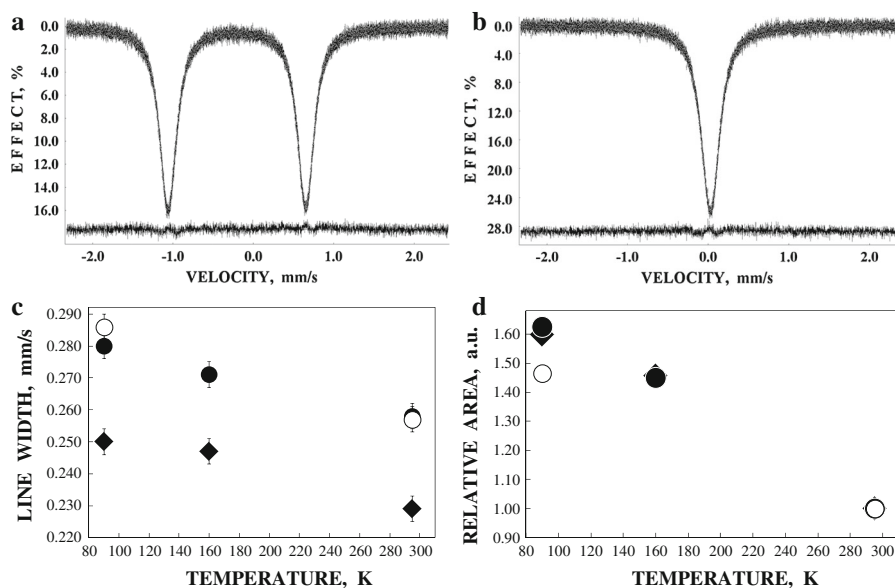
The spectra were also fitted using the UNIVEM-MS program with a least squares procedure and the Lorentzian line shape. Parameters determined for the measured spectra were isomer shift, quadrupole splitting, line width and spectrum area. The instrumental (systematic) error for each spectrum point and for the hyperfine parameters were  $\pm 0.5$  and  $\pm 1$  channel, respectively (Oshtrakh and Semionkin 2013). The error of the relative spectrum area did not exceed 10 %. If an error calculated with the fitting procedure (fitting error) for these parameters exceeded the instrumental (systematic) error, then we used the larger error instead. Values of the isomer shifts are given relative to that of  $\alpha\text{-Fe}$  at 295 K.

Additionally, we used the standard absorber of sodium nitroprusside (SNP) glued on the alumina foil free from iron (5 mg Fe/cm<sup>2</sup>) and potassium ferrocyanide (PFC) in the forms of powder packed into the sample holder, and the powder glued on the alumina foil free from iron (the iron surface density of the samples did not exceed 5 mg Fe/cm<sup>2</sup>). For the control

of cryostat vibrations (that may occur with temperature decrease as a result of nitrogen gas flow increase and also as a result of powdered particles vibration in the samples in spite of close packing), we measured Mössbauer spectra of SNP and both PFC samples at selected temperatures (see Fig. 1a, b) using Mössbauer spectroscopy with a high velocity resolution. These spectra were fitted using UNIVEM-MS program. The obtained line widths and normalized relative areas versus temperature are shown in Fig. 1c, d. It is clearly seen that there is no anomalous line broadening while approximately linear slope should be considered as a result of both cryostat vibrations and increase of the effective thickness due to increase in the Mössbauer effect probability ( $f$ -factor). We can point out that in the case of two PFC samples normalized relative spectrum area for glued powder was slightly smaller at 90 K than those for packed powder sample that may be a result of small amount of PFC lost during glued sample preparation. However, these spectral areas for both PFC samples demonstrated the absence of significant effect of particles vibrations.

## Results

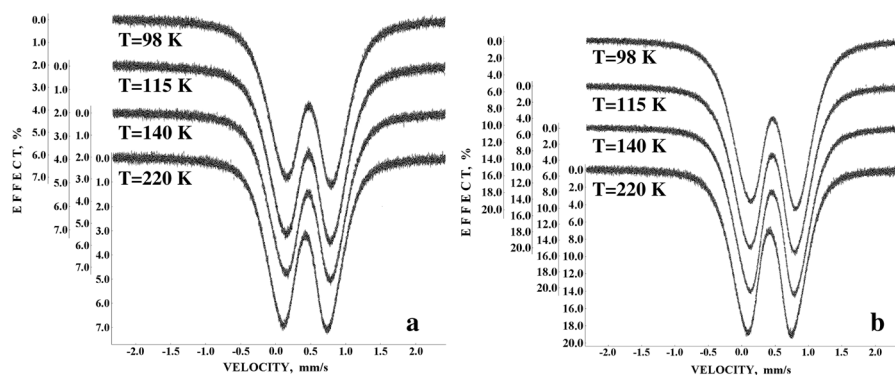
Mössbauer spectra of the ferritin and Ferrum Lek sample measured in the temperature range between 295 and 90 K displayed doublet shapes without any magnetic components (see, for instance, spectra presented in Fig. 2). First, the changes in the spectral shape were evaluated in a model-independent way, and then the spectra were fitted using one quadrupole doublet as the first approximation. Though a fit with one doublet cannot account for all the spectral features, this approach allowed us to derive approximations of the main Mössbauer parameters as functions of temperature and compare the results with a model-independent analysis. The main unexpected result was an unusual temperature dependence of the line width for both nanosized hydrous ferric oxide cores as shown in Fig. 3a. This was confirmed by the corresponding unusual temperature dependence of the  $\sigma$ , square root of the second central moment (Fig. 3b). The anomaly detected concerning the line width was found to be accompanied by a corresponding anomaly in the normalized relative spectral area versus temperature (Fig. 4). Temperature dependences of the central shift obtained from the model-independent analysis, and



**Fig. 1** Mössbauer spectra of the standard absorber SNP (a) and PFC powder (b) measured in 4096 channels at 160 K and line width (c) and relative area normalized to 295 K value (d) of

Mössbauer spectra of the standard absorber SNP (black diamond) and PFC powder (black circle) and glued powder (white circle) versus temperature

**Fig. 2** Mössbauer spectra of human liver ferritin (a) and Ferrum Lek (b) measured in 4096 channels at selected temperatures

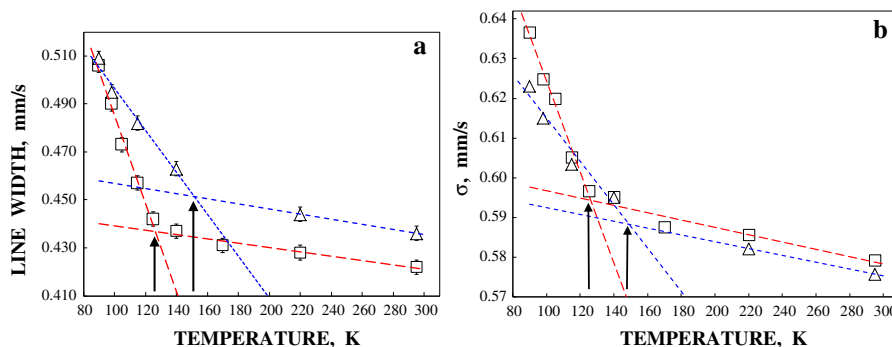


both isomer shift and quadrupole splitting obtained from the one doublet fit are shown in Fig. 5.

It is clearly seen that both the model-independent analysis and the one quadrupole doublet fit give similar results indicating unusual temperature dependence of Mössbauer parameters. With decreasing temperature, the anomaly starts to develop at a critical temperature  $T_0$  that may be approximated as the temperature of the intersection of straight lines fitted to the 'high' and 'low' temperature data as shown in Fig. 3. Temperatures at which these anomalies appear to be started are  $\sim 130$  K for Ferrum Lek with nanosized akaganéite core and  $\sim 150$  K for ferritin with nanosized ferrihydrite core.

## Discussion

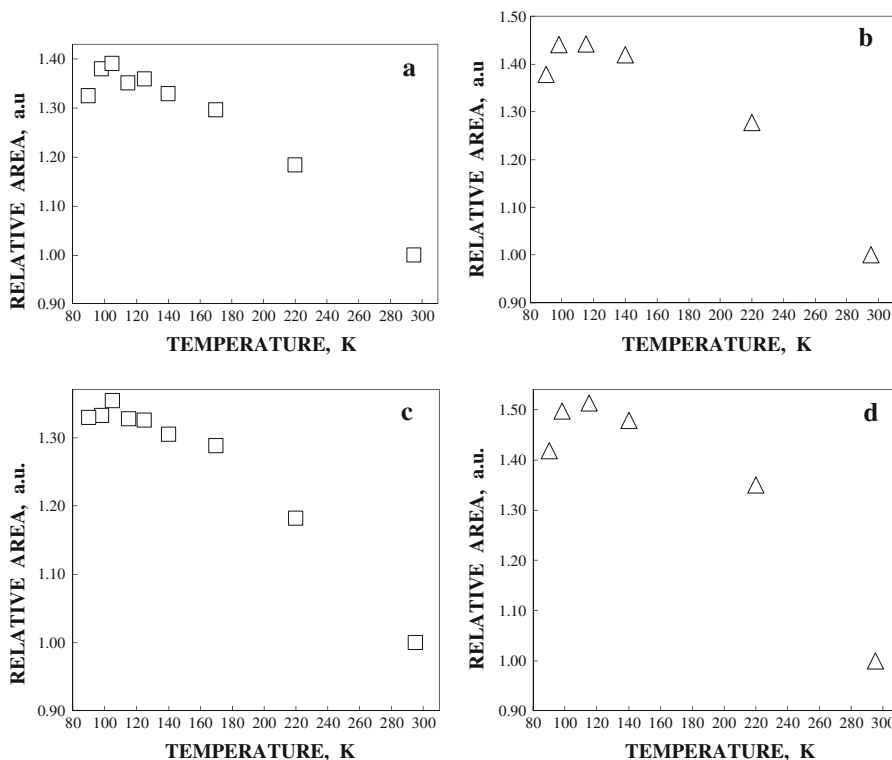
An earlier study of reconstituted horse spleen ferritin dynamics by Bauminger et al. (1987) demonstrated narrowing of Mössbauer line width at around 264 K that was not observed in our case. Another anomaly in the temperature dependence of  $f$ -factor for ferritin and its analogue polysaccharide iron complex (PIC) Niferex, both containing ferrihydrite and akaganéite cores, respectively, were observed at a temperature below 60 K by Mohie-Eldin et al. (1995). The authors explained their observation as being the result of magnetostriction which may be a reason of a decrease of  $f$ -factor at temperatures above 30 K for ferritin and



**Fig. 3** Unusual temperature dependence of the line width (a) and the  $\sigma$ , square root of the second central moment (b) for the Mössbauer spectra of nanosized hydrous ferric oxides cores in human liver ferritin (white up-pointing triangle) and in Ferrum Lek (white square). Indicated dashed lines represent

linear approximations for the data. Arrows indicate suggested temperatures of starting unusual behaviour of parameters. The standard error of  $\sigma$  is in the order of 0.001 mm/s and smaller than the symbols' size

**Fig. 4** Anomalous temperature dependence of the relative area normalized to 295 K value obtained from the model-independent analysis (a, b) and from the one doublet fit (c, d) of the Mössbauer spectra of nanosized hydrous ferric oxides cores in Ferrum Lek (white square) and in human liver ferritin (white up-pointing triangle). The error of the relative spectrum area did not exceed 10 % and smaller than the symbols' size

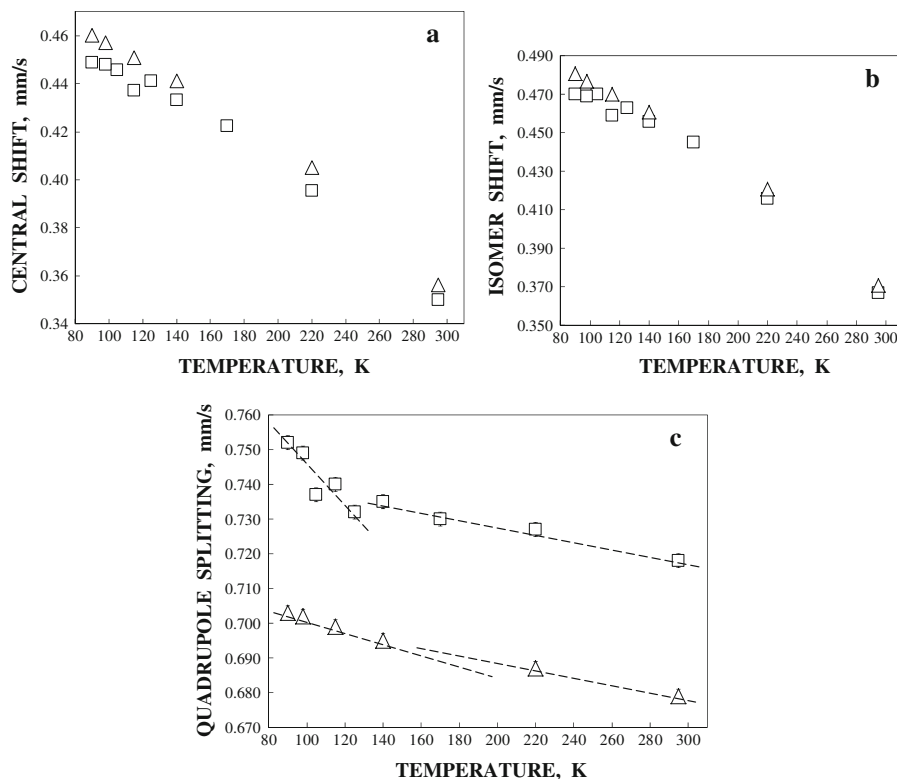


above 60 K for PIC. They excluded the effects of sample thickness and core motions inside protein shell while did not consider cryostat vibrations effect. However, the temperature dependence of the  $f$ -factor of ferritin obtained by Mohie-Eldin et al. (1995) was different from our result shown in Fig. 4b, d. In our case of ferrihydrite cores, there is a decrease of spectral area at 90 K in comparison with those at 98

and 115 K. As for akaganéite cores, in Fig. 4a, c, we also can see unusual dependence in the temperature range between 130 and 90 K.

One could consider that slowdown of fast magnetic relaxation in the superparamagnetic nanoparticles may be a reason of unusual line broadening in the Mössbauer spectra of nanosized hydrous ferric oxides cores in human liver ferritin and in Ferrum Lek below

**Fig. 5** Temperature dependences of the central shift obtained from the model-independent analysis (a) and isomer shift (b) and quadrupole splitting (c) obtained from the one doublet fit of the Mössbauer spectra of nanosized hydrous ferric oxides cores in human liver ferritin (*white up-pointing triangle*) and in Ferrum Lek (*white square*). Dashed lines indicate different slopes for quadrupole splitting temperature dependences. The standard error of  $\sigma$  and the instrumental (systematic) error of isomer shift are in the order of 0.001 mm/s and smaller than the symbols' size

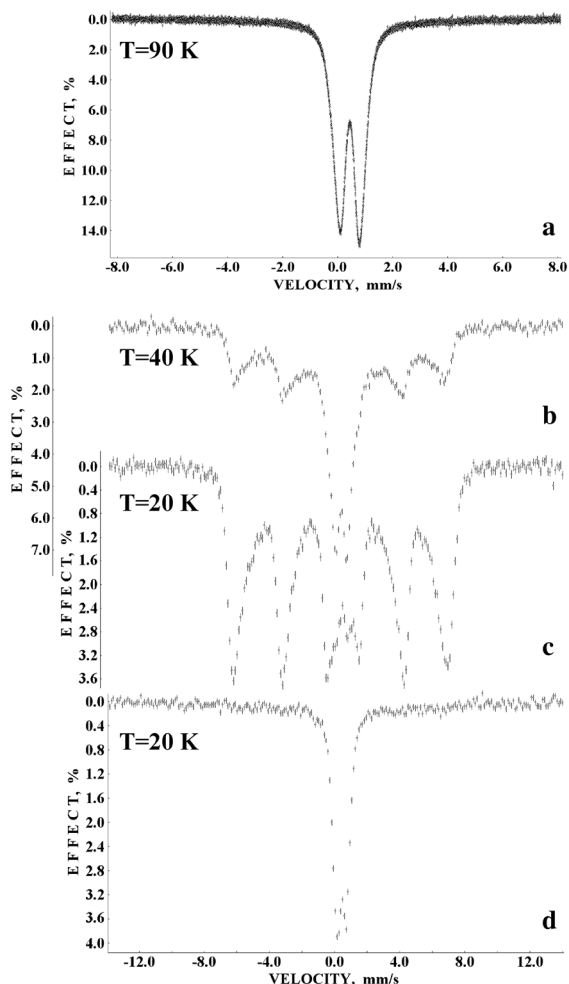


160 K. However, recently it was found that the anisotropy energy barrier for human liver ferritin was smaller than that for Ferrum Lek (Alenkina et al. 2013a; b), which would imply that the temperature at which the line broadening starts as the result of slowdown of magnetic relaxation should be higher for Ferrum Lek. In addition, the absence of magnetic hyperfine component in the 90 K spectrum of Ferrum Lek is clearly seen in Fig. 6a. Clear magnetically split components were observed in the Ferrum Lek spectra measured at 40 and 20 K, while in the 20 K Mössbauer spectrum of ferritin, the presence of a magnetic hyperfine component was not clear (Fig. 6b–d). In contrast, it is clearly seen in Fig. 3a that unusual line broadening starts for the ferritin at higher temperature than that for the Ferrum Lek. Therefore, we should exclude magnetic relaxation from the possible origins of this anomaly. At the same time, neither cryostat vibrations nor sample thickness can explain the anomalous line broadening shown in Fig. 3a, as they should both display linear temperature dependence in the temperature range 295–160 K, similar to that shown in Fig. 1c.

Mössbauer spectra of Ferrum Lek and ferritin measured at 80, 70 and 60 K displayed doublet shapes without magnetic components. Figure 7 shows the line width characteristic of these measurements evaluated on the basis of a one doublet fit (note that in these cases pumping vibrations contributed to the line broadening of the spectra). On the basis of these results, we can suppose a possible saturation of the line broadening effect in the temperature range of 80–60 K.

We hypothesize that the anomalous changes detected in the Mössbauer parameters of ferritin and Ferrum Lek are caused by a phase transition occurring in the range of 120–160 K, which influences the dynamic properties and the average positions of oxygen ions in the oxygen octahedra surrounding the iron ions. At higher temperatures excited vibrational modes of the oxygen octahedra may realize a fast enough relaxation of the electric field gradient (EFG) at the  $^{57}\text{Fe}$  nucleus to make only an averaged quadrupole splitting value observable in the Mössbauer spectra. With the temperature decreasing below  $\sim 130$  K, a slowdown of oxygen lattice vibrations

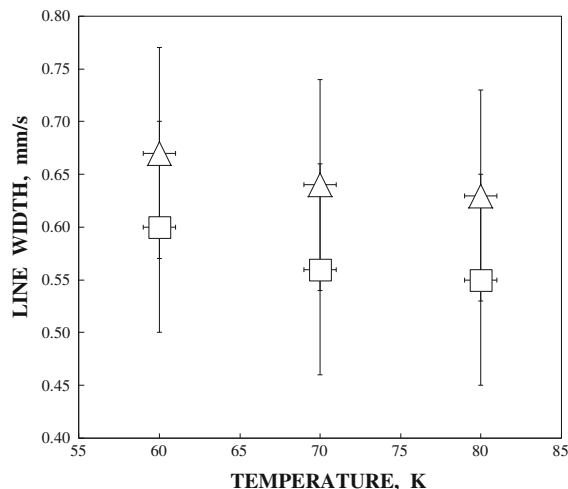




**Fig. 6** Mössbauer spectra of Ferrum Lek measured in a large velocity range in 4096 channels at 90 K (a) and in 250 channels at 40 K (b) and 20 K (c) and Mössbauer spectrum of ferritin measured in a large velocity range in 250 channels at 20 K (d)

may occur that gives gradually rise to the appearance of the different possible EFG levels instead of an averaged one. In the spectra, this may lead to an apparent broadening of the lines of the doublets as observed, as well as to a change in the magnitude of the apparent quadrupole splitting as clearly found for Ferrum Lek (Fig. 5). It is interesting to point out that earlier X-ray absorption fine structure study of ferritin iron core in frozen solution demonstrated considerable structural disorder at low temperatures down to 80 K, also indicating a possible phase transition (Heald et al. 1979).

The anomalies observed in the temperature dependences of the normalized relative spectral area and—



**Fig. 7** Temperature dependence of the line width obtained from the one doublet fit of the Mössbauer spectra of nanosized hydrous ferric oxides cores in Ferrum Lek (white square) and in human liver ferritin (white up-pointing triangle) measured with a low velocity resolution at 80, 70 and 60 K

to a lesser extent—in that of the isomer shift & central shift below  $\sim 130$  K may refer to an anomalous change in the vibrational state of the  $^{57}\text{Fe}$  nuclei, which corroborates the occurrence of a phase transition in this temperature range.

Taking into account some small structural differences between ferrihydrite and akaganéite, we can assume that ferrihydrite cores undergo such kind of microstructural rearrangements at higher temperatures (below  $\sim 150$  K), while akaganéite cores undergo similar microstructural rearrangements at lower temperatures (below  $\sim 130$  K).

### Conclusion

A formerly unknown anomaly has been discovered in the  $^{57}\text{Fe}$  Mössbauer parameters of ferritin and its pharmaceutical analogue Ferrum Lek at around  $T_0 \sim 150$  and  $\sim 130$  K, respectively. The anomaly is most clearly visualized in an enhanced rate of increase of the Mössbauer line width with decreasing temperature below  $T_0$ , as well as in an anomalous temperature dependence of the spectral area just below  $T_0$ . In addition, the quadrupole splitting and—to a lesser extent—the isomer shift also reflect the anomaly in around the same temperature interval. The anomaly can be interpreted as being the result of a phase

transition influencing the vibrational state of the oxygen octahedron surrounding iron ions, as well as that of the iron ions themselves. The anomalous increase of the line width with decreasing temperature was hypothesized to be caused by the slowing down of oxygen atomic vibrations and an associated slowdown in the relaxation of the EFG at the  $^{57}\text{Fe}$  nuclei.

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