



# Mössbauer spectroscopic study of a $\sigma$ -Fe<sub>65.9</sub>V<sub>34.1</sub> alloy: Curie and Debye temperatures



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## ARTICLE INFO

### Article history:

Received 2 October 2015

Received in revised form

8 December 2015

Accepted 8 December 2015

Available online 12 December 2015

### Keywords:

Fe–V intermetallic compounds

Sigma-phase

Mössbauer spectroscopy

Curie temperature

Debye temperature

## ABSTRACT

Sigma-phase Fe<sub>65.9</sub>V<sub>34.1</sub> alloy was investigated with the Mössbauer spectroscopy. Mössbauer spectra were recorded in the temperature interval of 80–330 K. Their analysis in terms of the hyperfine distribution protocol yielded the average hyperfine field,  $\langle B \rangle$ , the average center shift,  $\langle CS \rangle$ , and the spectral area, A. The magnetic ordering temperature,  $T_C = 312.5(5)$  K was determined from the temperature dependence of  $\langle B \rangle$ , and the Debye temperature,  $T_D$ , from the temperature dependence of  $\langle CS \rangle$  and the relative spectral area. The value obtained from the former was 403(17) K and that from the latter 374(2) K. The lattice dynamics of Fe atoms was described in terms of the kinetic,  $E_k$ , and the potential energy,  $E_p$ . The force constant for the Fe atoms vibrations was determined as 188 (6) N/m.

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## 1. Introduction

Sigma ( $\sigma$ ) phase belongs to the Frank-Kasper (FK) family of phases which are also designated as topologically close-packed (TCP) structures. Their characteristic features are high values (12–16) of coordination numbers [1]. An interest in  $\sigma$  (and other FK-phases) is twofold: on one hand it has practical reasons, and, on the other hand, scientific ones. The former interest stems from the detrimental effect of  $\sigma$  on many useful properties of technologically important materials e. g. steels, super alloys, high entropy alloys. Its presence, even in low percentage, significantly deteriorates useful properties like mechanical strength and resistance to high temperature corrosion e. g. Ref. [2]. In these circumstances, the interest in  $\sigma$  from the practical viewpoint is rather concentrated on efforts aimed at development of such materials in which its precipitation is suppressed or, at least, retarded. The scientific interest in  $\sigma$  is challenged by its complex crystallographic structure (tetragonal unit cell – space group  $D_{4h}^{14} - P4_2/mnm$  – with 30 atoms residing on 5 non-equivalent lattice sites), and interesting physical properties. They can be readily tailored by changing alloy elements and chemical composition thanks to the fact that  $\sigma$  can exist in a

certain composition range. Concerning magnetic properties of  $\sigma$  in the Fe–V system, one of the subjects of the present study, they were revealed in early 1960s [3], and until recently regarded as ferromagnetic. Not long ago, its magnetism was shown to be more complex than believed viz. it had turned out to have a re-entrant character [4]. The Fe–V system is especially interesting with regard to  $\sigma$ , as the phase can be formed within a wide range of composition viz. ~33 – ~65 at% V [5]. This gives a unique opportunity for changing physical properties of  $\sigma$  in a wide range of composition. Concerning the magnetic ones, the magnetic ordering temperature (Curie point),  $T_C$ , can be continuously raised up to above room temperature. The actual record obtained for the Fe<sub>65.6</sub>V<sub>34.4</sub> alloy is as high as ~307 K as determined from magnetization measurements and ~324 K as found from Mössbauer spectroscopic study [6].

Regarding the Debye temperature,  $T_D$ , of the  $\sigma$ -Fe<sub>100-x</sub>V<sub>x</sub> alloys ( $34.4 \leq x \leq 59$ ) so far it was determined only with the Mössbauer spectroscopy from a temperature dependence of the center shift [7]. The  $T_D$ -values span between ~420 and ~600 K and do not show any monotonous behavior.

This paper reports results on the Curie and Debye temperatures as determined using the Mössbauer spectroscopy on a  $\sigma$ -Fe<sub>65.9</sub>V<sub>34.1</sub> sample which, to our best knowledge, is the  $\sigma$ -FeV alloy with the lowest concentration of V investigated so far.

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## 2. Experimental

### 2.1. Sample preparation and characterization

Master alloy of a nominal composition  $\alpha$ -Fe<sub>66.5</sub>V<sub>33.5</sub> was prepared by melting 1323 mg of Fe (99.95% purity) and 609 mg of V (99.5% purity) in an arc furnace under protective argon atmosphere. A loss of mass caused by the melting was 2 mg which corresponds to an uncertainty in the concentration of  $\pm 0.1$  at%. The ingot was flipped over and remelted three times before it was solution treated at 1273 K for 72 h to increase its homogeneity. Finally, it was quenched onto a block of brass kept at 295 K. The transformation into the  $\sigma$ -phase was performed by annealing the solution-treated ingot at  $T = 973$  K for 14 days. The verification of the  $\alpha$ -to- $\sigma$  phase transformation was done on a powder sample by recording a room-temperature X-ray diffraction pattern – shown in Fig. 1 – using Cu-K $\alpha$  radiation ( $\lambda = 1.54053$  Å) and an Empyrean X-ray diffractometer from PANalytical. Its analysis with the FullProf software gave evidence that the master alloy was transformed into  $\sigma$  to 97.5(5)%. The untransformed residual phase (2.5%) was identified as  $\alpha$ -iron. Thus the stoichiometry of  $\sigma$  can be estimated as Fe<sub>65.9</sub>V<sub>34.1</sub>. The parameters of the unit cell of  $\sigma$  were found to be as follows:  $a = 8.8674(5)$  Å and  $c = 4.6015(4)$  Å. They are in line with those found previously for the alloys with higher contents of vanadium [7].

### 2.2. Mössbauer spectra measurements and analysis

Mössbauer spectra were recorded in a temperature range of 80–330 K using a standard spectrometer working in a constant acceleration mode. Gamma rays of 14.4 keV were supplied by a <sup>57</sup>Co source embedded into a Rh matrix. Examples of the spectra are presented in Fig. 2 (left panel). They are very similar in shape to those recorded previously on the  $\sigma$ -Fe<sub>65.6</sub>V<sub>34.4</sub> alloy [6]. The spectra were analyzed to yield spectral parameters pertinent to two quantities of interest viz. the magnetic ordering temperature (Curie),  $T_C$ , and the Debye temperature,  $T_D$ . The former can be readily determined from a temperature dependence of the average hyperfine field,  $\langle B \rangle$ , while the latter in two ways: from a temperature dependence of (a) the center shift, CS, and (b) relative recoil-free fraction,  $f/f_0$ .

Mössbauer spectra were analyzed using a least-square procedure and the transmission integral approach. All three hyperfine interactions were taken into account. Each spectrum was assumed

to be composed of five components (sub spectra) following the fact that Fe atoms occupy all five lattice sites in the unit cell of  $\sigma$ . The shape of each component was assumed to have the Voigt's profile [8]. Relative contributions of the components,  $W_k$ , were equal to the corresponding relative lattice site occupancies by Fe atoms as revealed from the neutron diffraction experiment [9]. They were kept constant in the fitting procedure. A center shift,  $CS_k$ , ( $k = 1, 2, 3, 4, 5$ ) of each component was a sum of the isomer shift,  $IS_k$ , characteristic of a given component (sub lattice) as reported elsewhere [10], and the so-called second order Doppler shift, SOD. The latter was common to all five components and treated as free parameter. The temperature dependence of the isomer shift is very weak [11], so it was neglected. Consequently, the entire temperature dependence of the center shift was ascribed to the temperature dependence of SOD. The latter can be used to determine the Debye temperature and the mean-square velocity of lattice vibrations – see Section 3.2.

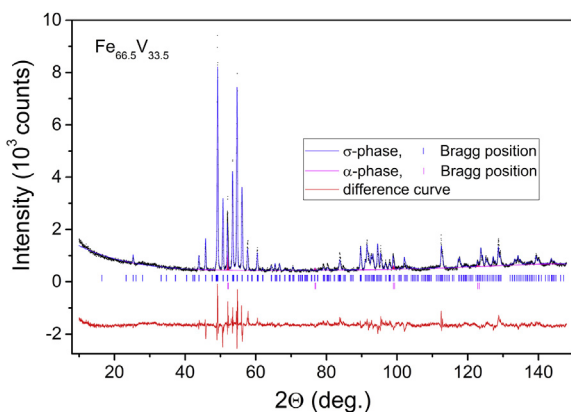
Magnetic properties of the particular lattice sites in the  $\sigma$ -FeV alloys (and other  $\sigma$ -phase alloys) have not been fully resolved yet. However, theoretical calculations [12] and <sup>51</sup>V NMR measurements [13] gave evidence that all five sub lattices contribute to the magnetism. Therefore, we assumed that each of the five components adds to the average hyperfine field,  $\langle B \rangle$ . The Gaussian distribution of the hyperfine field was assumed, and  $\langle B \rangle$  was obtained by integrating the five Gaussians. Examples of the hyperfine distribution curves received in this way are shown in Fig. 2, and the best-fit spectral parameters are displayed in Table 1.

## 3. Results and discussion

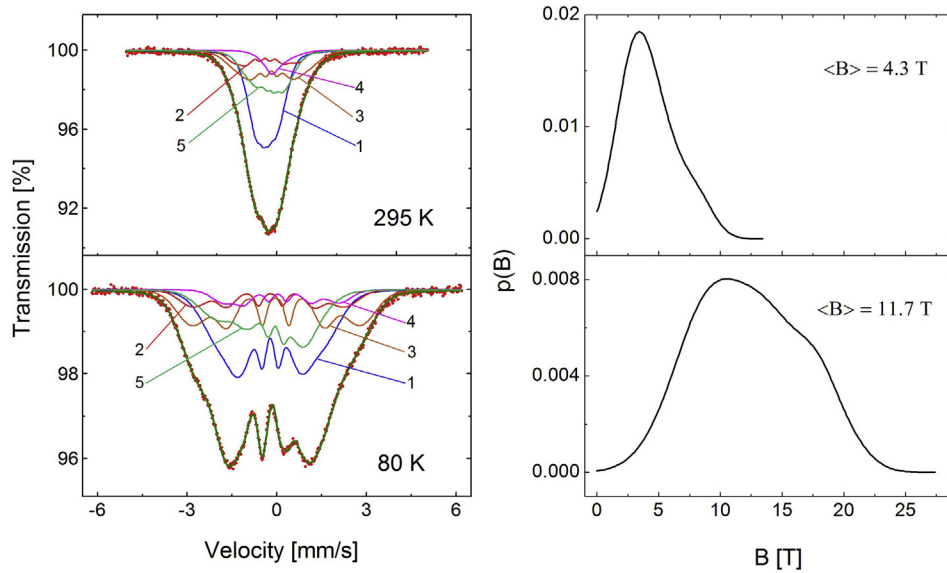
### 3.1. Curie temperature

Temperature dependence of  $\langle B \rangle$  is illustrated in Fig. 3. Two sets of data are displayed: (a) the presently measured ones, and (b) those reported in Ref. [6]. Both sets of the data were analyzed in terms of the Brillouin function. The best fit to the present data was achieved with the total angular momentum quantum number  $J = 3$  and yielded the magnetic ordering temperature of  $T_C = 312.4(5)$  K. The extrapolated to zero temperature value of  $\langle B \rangle = 12.07(5)$  T is equivalent to the magnetic moment of  $0.9 \mu_B$  using the conversion constant reported elsewhere [6].

It is evident from Fig. 3 that the  $\langle B \rangle(T)$  dependence as found in the present study is different than the one obtained for the  $\sigma$ -Fe<sub>65.6</sub>V<sub>34.4</sub> alloy [6]. The largest difference exists in the value of  $T_C$  which for the presently studied sample is by  $\sim 12$  K lower. Another difference occurs in the temperature interval of  $\sim 80$ – $200$  K in which the presently determined values of  $\langle B \rangle$  are higher than the corresponding ones reported previously [6]. There is also a difference in the value of  $J$  which in the case of the  $\sigma$ -Fe<sub>65.6</sub>V<sub>34.4</sub> sample was equal to 3.5. The differences in the  $\langle B \rangle(T)$  behavior can be understood in terms of a different (a) concentration of V, (b) degree of chemical homogeneity, and/or (c) site occupancy in the two alloys. The (b) and (c) effects can have its origin in various conditions applied for the  $\alpha \rightarrow \sigma$  phase transformation. Following the  $T_C(x)$  – relationship for the  $\sigma$ -FeV alloys viz. an increase of  $T_C$  at the rate of  $\sim 10$  K per at% Fe in the range of  $\sim 34.4$ – $40$  at% V [6], one would expect  $T_C \approx 325$  K for the  $\sigma$ -Fe<sub>65.9</sub>V<sub>34.1</sub> alloy, whereas  $T_C = 312.5$  K was presently determined from the  $\langle B \rangle(T)$  plot. The Mössbauer spectroscopy, being a microscopic method, gives information on local atomic configurations usually within the radius of two neighbor shells around the probe nuclei. Therefore, spectral parameters including the hyperfine field may have different values for samples having different degree of the homogeneity and/or variations in the lattice sites occupancy. On the other hand, magnetization,  $M$ , as a macroscopic method is much less, if ever, sensitive to



**Fig. 1.** The Rietveld refinement XRD pattern of Fe<sub>66.5</sub>V<sub>33.5</sub> alloy recorded at room temperature. Positions of peaks of the  $\sigma$  and  $\alpha$  phases are indicated by vertical bars in black and red, respectively. A difference curve between the measured and the calculated patterns is also displayed. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

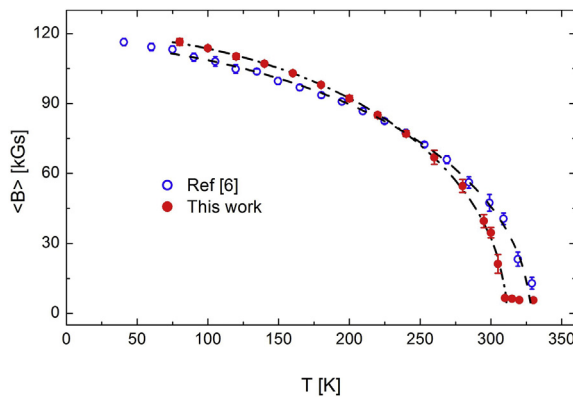


**Fig. 2.** (left panel) Mössbauer spectra recorded on the  $\sigma$ -Fe<sub>65.9</sub>V<sub>34.1</sub> alloys at selected temperatures shown (the five contributing components are indicated), (right panel) corresponding curves of the hyperfine field distribution.

**Table 1**

The best-fit spectral parameters as obtained with the applied fitting procedure for two extreme temperatures. Values of the center shift, CS, are given relative to  $\alpha$ -Fe at RT.  $V_{zz}$  stands for the main component of the electric field gradient.

Component no.	Component contribution [%]	CS [mm/s]		B [kGs]		$V_{zz}$ [ $10^{22}$ V/m <sup>2</sup> ]	
		T = 295 K	T = 80 K	T = 295 K	T = 80 K	T = 295 K	T = 80 K
1	39.2	−0.241(2)	−0.099(2)	29(2)	97.4(6)	0.01(2)	0.014(3)
2	9.8	−0.274(2)	−0.132(2)	64(2)	151.6(9)	0.019(3)	−0.028(8)
3	22.6	−0.065(2)	0.077(2)	68(3)	165.8(7)	0.007(8)	0.010(3)
4	6.6	−0.059(2)	0.201(2)	20(2)	114.2(9)	0.09(6)	0.060(7)
5	21.8	−0.150(2)	−0.132(2)	41(5)	87.6(9)	−0.04(1)	−0.181(5)



**Fig. 3.** Average hyperfine field,  $\langle B \rangle$ , vs. temperature,  $T$ , as determined for (a) the presently studied sample (full symbols), and (b) the one reported in Ref. [6] (open symbols). The lines stand for the best fits to the data in terms of the Brillouin function.

the above-mentioned factors. The  $T_C$ -values derived from  $M(T)$  behavior should reflect difference in the chemical composition, if any, rather than the ones in the chemical homogeneity and site occupancy. It should be added that the presently found value of  $T_C$  perfectly agrees with the one determined from the AC magnetic susceptibility measurements for the same alloy [14]. The latter is, however, by  $\sim 5$  K higher than  $T_C$  determined from  $M(T)$  measurements performed on the  $\sigma$ -Fe<sub>65.4</sub>V<sub>34.4</sub> sample [6] i.e. it is in line with the general trend observed for other compositions [6]. Thus, the

higher (by  $\sim 5$  K) value of  $T_C$  found in the present experiment would correspond to a lower content (by  $\sim 0.5$  at%) of V. In other words, the concentration of V in the  $\sigma$ -phase of the presently studied alloy is slightly lower than that in the  $\sigma$ -Fe<sub>65.6</sub>V<sub>34.4</sub>.

### 3.2. Debye temperature

#### 3.2.1. Temperature dependence of center shift

The temperature dependence of the center shift,  $CS(T)$ , can be expressed by the following equation:

$$CS(T) = IS(0) - \frac{3k_B T}{2mc} \left[ \frac{3T_D}{8T} + \left( \frac{T}{T_D} \right)^3 \int_0^{T_D/T} \frac{x^3}{e^x - 1} dx \right] \quad (1)$$

Where  $IS(0)$  stays for the isomer shift (temperature independent),  $k_B$  is the Boltzmann constant,  $m$  is a mass of  $^{57}\text{Fe}$  atoms.

The second term in Eq. (1), known as the second-order Doppler shift,  $SOD$ , depends on the mean-squared velocity of the vibrating atoms,  $\langle v^2 \rangle$ , via the following equation:

$$SOD = -\frac{E_\gamma}{2c^2} \langle v^2 \rangle \quad (2)$$

Where  $E_\gamma$  stands for the energy of  $\gamma$ -rays (here 14.4 keV) and  $c$  is the velocity of light.

The dependence of the average center shift,  $\langle CS(T) \rangle = \sum_{k=1}^5 W_k CS_k$ , as found in the present study is illustrated in Fig. 4. The best-fit of Eq. (1) to the measured data, shown in Fig. 4 as a solid line, yielded  $T_D = 403(17)$  K.

### 3.2.2. Temperature dependence of recoil-free fraction

The recoil-free fraction,  $f$ , also known as the  $f$ -factor, can be written as follows:

$$f = \exp \left[ - \left( \frac{E_R}{\hbar c} \right)^2 \langle x^2 \rangle \right] \quad (3)$$

Where  $\langle x^2 \rangle$  is the mean-square amplitude of vibrating atoms. It is related to  $T_D$  via the following expression:

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

Where  $E_R = \frac{E_\gamma^2}{2mc^2}$  is the recoil energy.

In the approximation of a thin absorber, the  $f$ -factor is proportional to a spectral area,  $A$ . In practice one uses a normalized spectral area,  $A/A_0$ , as a measure of the relative  $f$ -factor,  $f/f_0$  ( $A_0$  being the spectral area at the lowest temperature – 80 K in this case).

The temperature dependence of  $\ln(f/f_0)$  is presented in Fig. 5. A good agreement between the experimental data and its fit in terms of Eq. (4) is evident, and the resulting value of the Debye temperature is equal to 374(2) K. This value of  $T_D$  is significantly lower than the one obtained from the  $CS(T)$  relationship. It is, however, known that the value of the Debye temperature depends, in general, on a method used for its determination, and it can vary significantly. Although in the present case we used the same method for determining the Debye temperature it was determined using two different spectral quantities viz.  $CS$  and  $f$ . They give different information on the lattice dynamics i.e. the former on the mean-square velocity, hence a kinetic energy,  $E_k$ , and the latter on the mean-square displacement, hence on the potential energy,  $E_p$ , of the vibrating atoms. Consequently, values of  $T_D$  as determined from  $CS$  and  $f$  are usually different. For example, in metallic iron  $T_D = 421(30)$  K was found from  $CS$  whereas  $T_D = 358(18)$  K from  $f$  [15].

### 3.3. Energy relations

#### 3.3.1. $\langle v^2 \rangle - \langle x^2 \rangle$ correlation

As evidenced in Fig. 6 the mean-square velocity of vibrating Fe

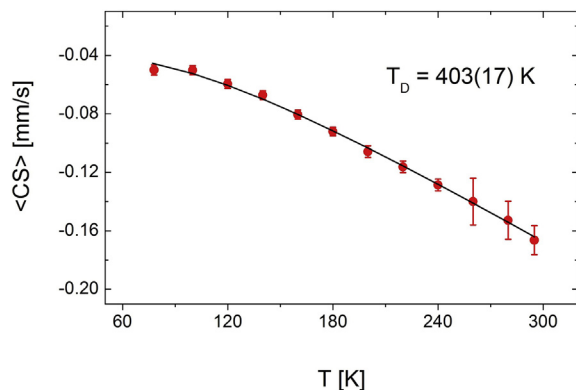


Fig. 4. Temperature dependence of the average center shift,  $\langle CS \rangle$ . The solid line represents the best fit of Eq. (1) to the data.

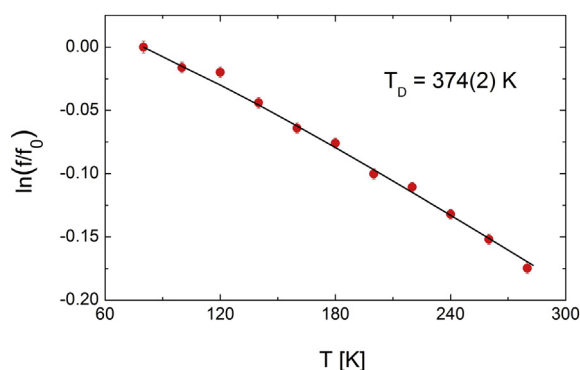


Fig. 5. Temperature dependence of  $\ln(f/f_0)$  and its best fit to Eq. (4) shown as a solid line.

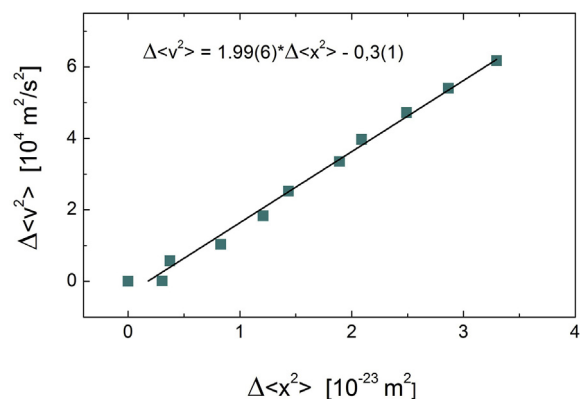


Fig. 6. Relationship between the mean-square velocity of the vibrating Fe atoms,  $\langle v^2 \rangle$ , and the mean-square amplitude of these vibrations,  $\langle x^2 \rangle$ . The solid line represents the best linear fit to the data.

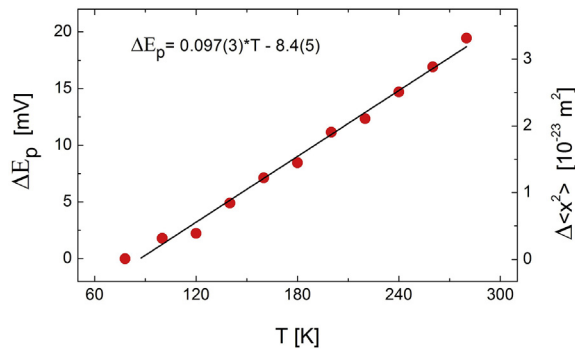
atoms,  $\langle v^2 \rangle$ , is linearly correlated with the corresponding mean-square amplitude,  $\langle x^2 \rangle$ . The force constant,  $D$ , can be calculated based on this correlation. Namely,  $D = m \cdot \alpha$ , where  $\alpha$  is the slope of the best-fit line in the  $\langle v^2 \rangle - \langle x^2 \rangle$  relationship, and  $m$  is the mass of  $^{57}\text{Fe}$  atoms. In this way the value of  $D = 188(6)$  N/m was found. It compares reasonably well with the value of 157(2) N/m derived from the partial density of states measured at 298 K for a  $\sigma\text{-Fe}_{52.5}\text{Cr}_{47.5}$  alloy [16]. The obtained  $D$ -value can be next used to calculate the potential energy,  $E_p = 0.5 \cdot D \cdot \langle x^2 \rangle$ .

#### 3.3.2. $\langle x^2 \rangle$ and potential energy

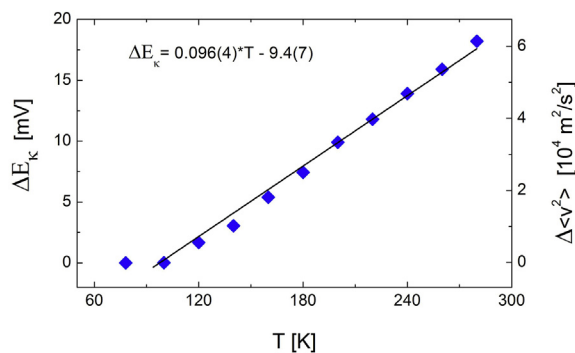
The knowledge of  $f/f_0$  enables, via Eq. (3), determination of a relative change of the mean-square amplitude of vibrating atoms,  $\Delta \langle x^2 \rangle = \langle x^2 \rangle - \langle x_0^2 \rangle$ , and, in turn, a relative temperature-induced change of the potential energy,  $\Delta E_p = 0.5 \cdot D \cdot \Delta \langle x^2 \rangle$ . Its dependence on temperature is linear as shown in Fig. 7.

#### 3.3.3. $\langle v^2 \rangle$ and kinetic energy

The Eq. (2) enables determination of the mean-square velocity of the vibrating Fe atoms,  $\langle v^2 \rangle$ , hence that of the kinetic energy,  $E_k = 0.5 \cdot m \cdot \langle v^2 \rangle$ . As we want to compare it with the potential energy of the vibrations which, in the present experiment, can be determined only relatively – see the previous paragraph – we will determine a change of the kinetic energy,  $\Delta E_k = 0.5 \cdot m \cdot (\langle v^2 \rangle - \langle v_0^2 \rangle)$ , relative to its value at the lowest measured temperature,  $E_{ok} = 0.5 \cdot m \cdot \langle v_0^2 \rangle$ . Such obtained  $\Delta E_k$ -values as well as the  $\Delta \langle v^2 \rangle = (\langle v^2 \rangle - \langle v_0^2 \rangle)$  ones are plotted in Fig. 8. The best-linear fit to the data is shown as well.



**Fig. 7.** Relative change of the potential energy,  $\Delta E_p$ , and of the mean-square amplitude of vibrating atoms,  $\Delta \langle x^2 \rangle$ , as a function of temperature,  $T$ . The solid line stands for the best linear fit to the data.



**Fig. 8.** Relative change of the kinetic energy,  $\Delta E_k$ , and of the mean-squared velocity of vibrating atoms,  $\Delta \langle v^2 \rangle$ , as a function of temperature,  $T$ . The solid line stands for the best linear fit to the data.

### 3.3.4. Kinetic vs. potential energy

The plots of  $\Delta E_k$  and  $\Delta E_p$  versus temperature show here a very similar and a regular behavior viz. both increase linearly with  $T$ . This is in contrast to the results found for the  $\sigma$ -Fe<sub>100-x</sub>Cr<sub>x</sub> ( $x = 46, 48$ ) alloys, where the changes in  $E_p$  were up to one order of magnitude higher than the corresponding ones in  $E_k$  and their temperature dependence was anomalous [17]. The difference is possibly due to the fact that in the present case the temperature of measurements covers one magnetic phase, while for the  $\sigma$ -Fe<sub>100-x</sub>Cr<sub>x</sub> alloys the

temperature where the anomaly was revealed was much lower (5–35 K) and it covered the temperature range in which a reentrant i.e. ferromagnetic-to-spin glass transition occurred. A departure from the harmonic behavior observed in this system could be due to a different degree of a spin-phonon coupling in the ferromagnetic and in the spin glass phases.

## 4. Conclusions

The results obtained in the present study permit the following conclusions to be drawn:

1. The  $\sigma$ -Fe<sub>65.9</sub>V<sub>34.1</sub> alloy orders magnetically at  $T_C = 312.5(5)$  K
2. The Debye temperature is equal to 403(17) K as found from the temperature dependence of the center shift, and to 374(23) K as determined from the temperature dependence of the relative spectral area.
3. The force constant responsible for the vibrations of Fe atoms is equal to 188(6) N/m.
4. Both kinetic as well as the potential energy increase linearly with temperature, and the rate of increase is the same which means that the vibrations of Fe atoms are harmonic.

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