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2010 J. Phys.: Condens. Matter 22 055402

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Debye temperature of disordered bcc-Fe–Cr alloys

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Received 14 October 2009, in final form 16 December 2009

Published 15 January 2010

Online at stacks.iop.org/JPhysCM/22/055402

Abstract

The Debye temperature, Θ_D , of $\text{Fe}_{100-x}\text{Cr}_x$ disordered alloys with $0 \leq x \leq 99.9$ was determined from the temperature dependence of the centre shift of ^{57}Fe Mössbauer spectra recorded in the temperature range of 60–300 K. Its compositional dependence shows an interesting non-monotonous behaviour. For $0 < x \leq \sim 45$, as well as for $\sim 75 \leq x \leq \sim 95$, the Debye temperature is enhanced relative to its value of a metallic iron, and at $x \approx 3$ there is a local maximum having a relative height of $\sim 12\%$ compared to a pure iron. For $\sim 45 \leq x \leq \sim 75$ and for $x \geq \sim 95$ the Debye temperature is smaller than the one for the metallic iron, with a local minimum at $x \approx 55$ at which the relative decrease of Θ_D amounts to $\sim 12\%$. The first maximum coincides quite well with that found for the spin-waves stiffness coefficient, D_o , while the pretty steep decrease observed for $x \geq \sim 95$, which is indicative of a decoupling of the probe Fe atoms from the underlying chromium matrix, is likely related to the spin-density waves which constitute the magnetic structure of chromium in that interval of composition and show also anomalous dynamic behaviour. The harmonic force constant calculated from the effective Debye temperature of the least Fe-concentrated alloy ($x \geq 99.9$) amounts to only 23% of the one characteristic of a pure chromium as determined from the heat capacity experiment.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

$\text{Fe}_{100-x}\text{Cr}_x$ alloys have been both of scientific and technological interest. The former follows, among others, from the fact that they can be regarded as a model system for studying various physical properties, e.g. magnetic ones, and testing appropriate theoretical models. The latter stems from the fact that the alloys represent a basic ingredient for a production of stainless steels that, due to their excellent properties, find a wide application in various branches of industry [1, 2]. One of the characteristic features of the Fe–Cr alloys is also that they form a solid solution within the whole concentration range while keeping the same (bcc) crystallographic structure. This is very important as it enables studying the effect of composition on various physical properties in a wide range within the same structure. In particular, as illustrated in figure 1, the lattice constant, for $0 \leq x \leq \sim 30$ shows some deviation from the

behaviour expected from Vegard's law, while it follows it quite well for $x \geq \sim 30$.

The Curie, T_C , and the Néel temperatures, T_N , are, in general, as schematically presented in figure 2, monotonous functions of the composition, as is the average magnetic moment, neglecting a shallow maximum observed in the Fe-rich alloys [4–6].

On the other hand, other quantities characteristic of the Fe–Cr system, show a non-monotonous character. As an example, the modulus of the average ^{119}Sn hyperfine field, $|\langle B \rangle|$, as a function of chromium content, x , for $\text{Fe}_{100-x}\text{Cr}_x$ alloys is presented in figure 3. The plot has been made using the experimental data published elsewhere [8].

The aim of this study was to reveal the effect of composition on the Debye temperature, Θ_D , which is justified by the lack of a reliable and systematic study of this quantity in the Fe–Cr system. In addition, the Debye temperature determined from low temperature specific heat measurements for several samples showed an irregular behaviour with a

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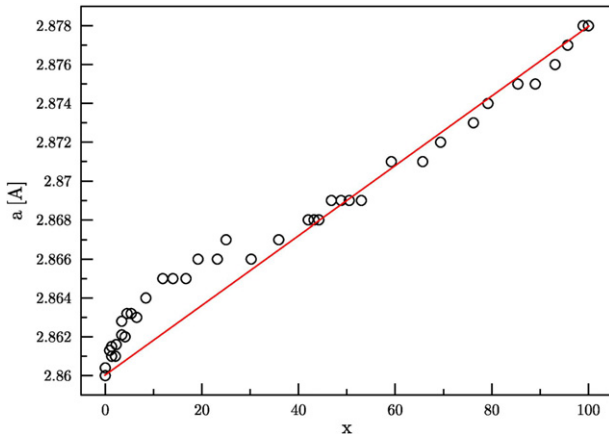


Figure 1. Lattice constant, a , versus chromium concentration, x , for $\text{Fe}_{100-x}\text{Cr}_x$ alloys, according to [3]. The straight line stands for the behaviour following Vegard's law.

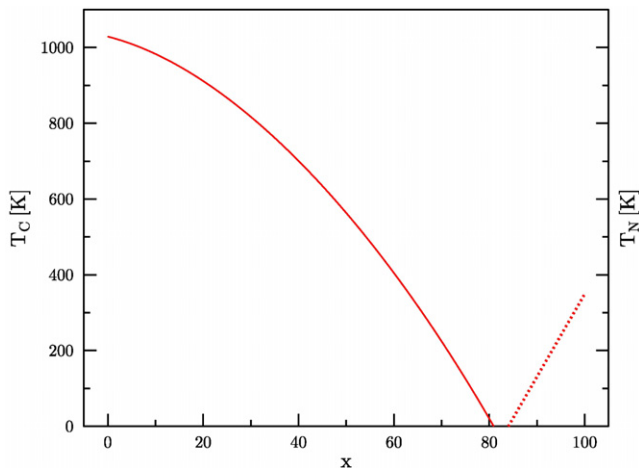


Figure 2. The Curie temperature, T_C , (full line and left-hand scale) and the Néel temperature, T_N , (dotted line and right-hand scale) versus chromium content, x , for $\text{Fe}_{100-x}\text{Cr}_x$ alloys. The plot has been made based on the experimental data published elsewhere [7].

difference in Θ_D as high as 374 K for $x = 80$ and 63 [9], which was not confirmed by similar measurements conducted in the temperature range of 133–623 K [10]. It should, however, be remembered that the actual value of Θ_D depends on the particular method applied to determine it, which reflects the fact that the Debye temperature is not a physical quantity but rather a parameter introduced to describe lattice dynamics via the Debye model. The sensitivity of Θ_D to the method applied to determine it follows from the fact that the phonon density of states (PDOS) in a real system has a much more complex shape than a parabola, and various experimental methods measure different parts of the PDOS resulting in different Θ_D -values. To illustrate this issue let us consider the extreme cases for the presently investigated system, i.e. $x = 0$ (pure Fe) and $x = 100$ (pure Cr). Concerning the former Θ_D ranges between 477 K, as determined from the elastic constant [11], and 418 K, as estimated from the x-ray diffraction experiment [12]. Regarding the latter, the amplitude of differences in Θ_D is even larger, as it spans between 630 K, as known from the specific

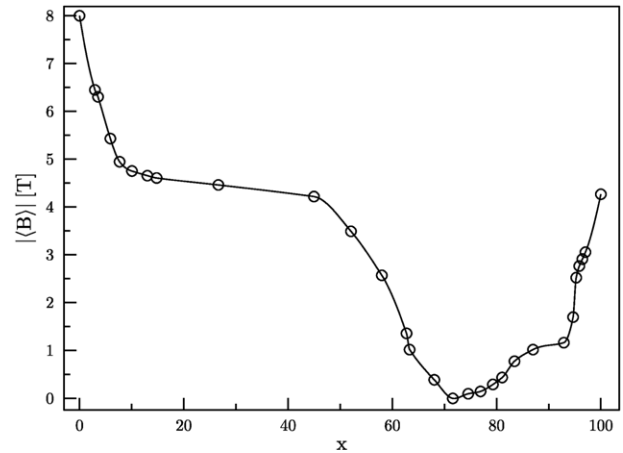


Figure 3. The modulus of the average ^{119}Sn hyperfine field, $|\langle B \rangle|$, as a function of chromium content, x , for $\text{Fe}_{100-x}\text{Cr}_x$ alloys, based on the experimental data published elsewhere [8].

heat measurements [13], and 466 K, as found from Young's modulus [14]. Consequently, a comparison of Θ_D -values obtained for a given sample by means of different methods seems not to be reasonable. Consequently, a systematic study of a given system with one particular method makes much more sense, and an eventual comparison between the results obtained with various methods should be done on the basis of normalized Θ_D -values. The latter procedure is applied in this paper.

2. Experimental details

For the present study our previously fabricated microcrystalline samples of Fe–Cr alloys [15, 16] as well as some new, and similarly prepared, ones were used. The Cr-rich alloys were made with iron in the form of a $\sim 95\%$ -enriched ^{57}Fe isotope in order to record good quality spectra in a reasonable time. The Debye temperature was determined by means of Mössbauer spectroscopy. For that purpose a series of Mössbauer spectra was recorded in a transmission geometry for each sample in the temperature range of 60–300 K, using a standard spectrometer and a $^{57}\text{Co}/\text{Rh}$ source of 14.4 keV gamma rays. The temperature of the samples, which were kept in a cryostat, was stabilized with an accuracy of ± 0.2 K. Examples of the recorded spectra, both as a function of composition as well as temperature, are shown in figures 4 and 5.

3. Results and discussion

The measured spectra were fitted to get an average value of the centre shift, (CS), which is one of the two pertinent quantities for determining Θ_D by means of Mössbauer spectroscopy [17, 18]. The spectra with a well-resolved structure were fitted assuming that a given spectrum consists of a number of six-line pattern subspectra, each of them corresponding to a particular atomic configuration around the probe ^{57}Fe nucleus, (m, n), where m is a number of Cr atoms in the first neighbour shell (NN), and n is a number of

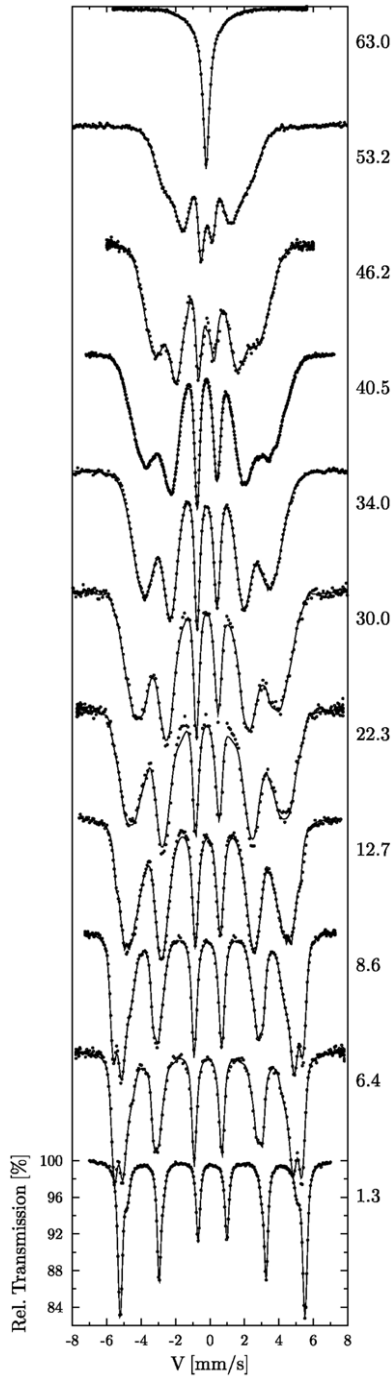


Figure 4. Room temperature Mössbauer spectra recorded on $\text{Fe}_{100-x}\text{Cr}_x$ samples labelled with various x -values. The solid lines are the best-fit to the experimental data.

Cr atoms in the next neighbour shell (NNN). It was further assumed that the effect of neighbouring Cr atoms on spectral parameters (hyperfine field, and centre shift) was additive. Using this procedure, which has proved successful and is described in detail elsewhere [15, 16], the average centre shift, (CS), could be calculated. The spectra with a poorly resolved structure were fitted in terms of the hyperfine field distribution method [19]. Following the experimental results [16], a linear correlation between the hyperfine field and the isomer shift

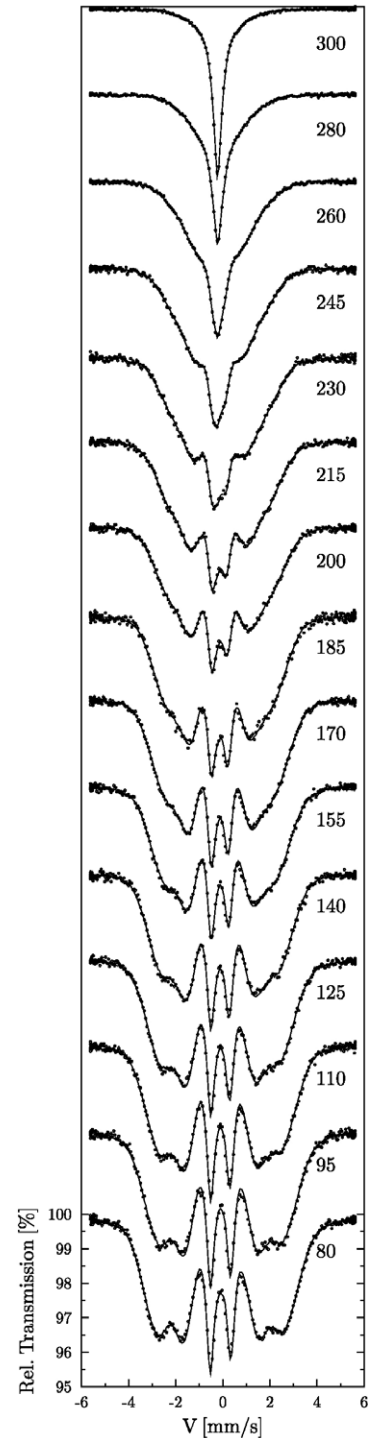


Figure 5. Mössbauer spectra recorded on a $\text{Fe}_{37}\text{Cr}_{63}$ sample at different temperatures (in kelvin) shown. Solid lines represent the best-fits to the experimental spectra.

was assumed in the fitting procedure. Finally, the spectra corresponding to a paramagnetic phase (Cr-rich samples) were analysed in terms of one Lorentzian-shaped line. The Debye temperature for each sample was next evaluated from the temperature dependence of (CS) determined in the above-described ways, using the following equation:

$$\langle \text{CS} \rangle (T) = \text{IS}(T) + \text{SODS}(T) \quad (1)$$

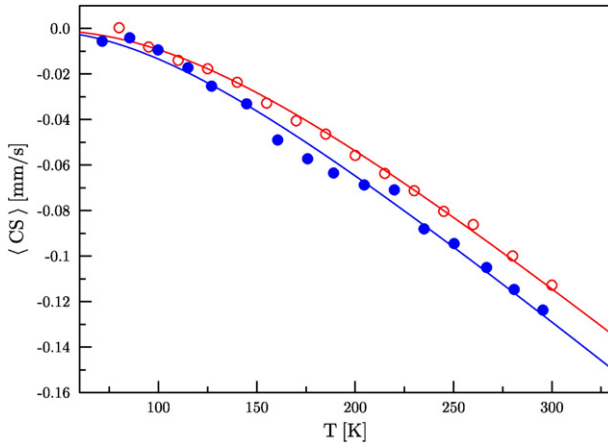


Figure 6. Dependence of the average central shift, $\langle CS \rangle$, on temperature for $Fe_{100-x}Cr_x$ alloys with $x = 53.15$ (full circles) and $x = 3.2$ (open circles). The solid line represents the best-fit to the experimental data in terms of equation (2).

where $IS(T)$ is the isomer shift, which is related to the charge density at the probe nucleus. Its temperature dependence, as discussed in [20], is generally speaking complex, and much weaker than that of the second term [21], so in practice it is usually neglected, i.e. approximated by a constant term, $IS(0)$. The latter may eventually be, however, composition dependent. SODS is the so-called second-order Doppler shift, which shows a strong temperature dependence. Assuming the whole temperature dependence of $\langle CS \rangle$ goes via the SODS term and using the Debye model for the phonon spectrum, one arrives at the following formula relating $\langle CS \rangle$ to Θ_D :

$$\langle CS(T) \rangle = IS(0) - \frac{3kT}{2Mc} \left[\frac{3\Theta_D}{8T} + 3 \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^3}{e^x - 1} dx \right] \quad (2)$$

where M is the mass of the ^{57}Fe nucleus, k is the Boltzmann constant, and c is the velocity of light.

Fitting equation (2) to the $\langle CS \rangle(T)$ -values (whose typical behaviour is illustrated in figure 6), determined by the procedures described above, enabled determination of the Θ_D -values which are displayed in table 1. In order to discuss them further and compare them with the data available in the literature, we use normalized data. For that purpose the ones found in the present study have been divided by 426 K ($\Theta_D = 426$ K was found for a pure Fe) and those determined with other methods were divided by the corresponding Θ_D -value of iron as found with that method. (For example by 445 K in the case of the specific heat measurements.) The normalized Debye temperature obtained in such way, Θ_D^* , is displayed in figure 7 as a function of the chromium concentration, x , the lattice constant, a , and the unit cell volume, V .

Let us start the discussion with the extreme cases i.e. those for $x = 0$ and 100. They clearly illustrate the well-known fact that the value of Θ_D depends on the method applied to determine it, as discussed in section 1. In the case of Mössbauer spectroscopy, there are even two ways of determining Θ_D from the same series of measurements i.e. one from the Lamb–Mössbauer factor, f , which is related

Table 1. Debye temperature, Θ_D , and its error, $\Delta\Theta_D$, as determined in the present study for disordered bcc- $Fe_{100-x}Cr_x$ alloys. The sample of $Fe_{37}Cr_{63}$ was measured twice: in a strain-free (no 14) and in a strain (no 15) condition.

No	x (at.%)	Θ_D (K)	$\Delta\Theta_D$ (K)
1	0	426	14
2	1.3	457	11
3	3.2	482	13
4	6.4	452	9
5	8.6	439	11
6	12.7	471	16
7	22.3	463	29
8	30.0	433	25
9	34.0	473	15
10	40.5	447	13
11	46.2	412	16
12	47.8	411	29
13	53.15	380	24
14	63.0	397	19
15	63.0	419	15
16	68.0	423	44
17	72.8	377	24
18	75.0	427	13
19	75.8	413	17
20	80.0	472	14
21	86.7	470	20
22	90.75	479	16
23	93.0	482	26
24	96.0	507	18
25	97.0	470	7
26	98.0	474	11
27	99.0	467	18
28	99.9	395	14

to the square displacement of the vibrating atoms from the equilibrium position, and the other from the centre shift, CS, which is related to their square velocity via the second-order Doppler shift. As is evident in figure 7 for pure iron, the Θ_D -values obtained from the two quantities are significantly different. This, in turn, illustrates well the fact that a comparison of the Debye temperature obtained not only with different techniques but also with the same, but based on different physical quantities, must be done and interpreted with caution. Consequently, a comparison of the normalized Θ_D -values, Θ_D^* , rather than the absolute ones, being more justifiable and reasonable, is done in this paper.

It is evident that the data obtained with the present study show a complex, non-monotonous character as a function of all three parameters, namely x , a and V . As there is no significant difference in the three plots displayed in figure 7, we will limit our discussion to the dependence of $\Theta_D^*(x)$. In general, one can distinguish concentrations for which there is an enhancement of Θ_D relative to its value for pure iron, i.e. $\Theta_D^* > 1$, and concentrations for which there is a diminution of Θ_D , i.e. $\Theta_D^* < 1$. In particular, the former exist for (A) $0 < x < \sim 45$ and (B) $\sim 75 < x < \sim 95$, while the latter apply for (C) $\sim 45 < x < \sim 75$ and (D) $x > \sim 95$. The enhancement in (A), which is discussed in more detail elsewhere [25], is correlated with the behaviour of the spin-waves stiffness constant, D_o . The minimum in Θ_D^* observed around the equiatomic composition agrees pretty well with the concentration at which the Fe–Cr alloys are thermodynamically unstable and, on heating,

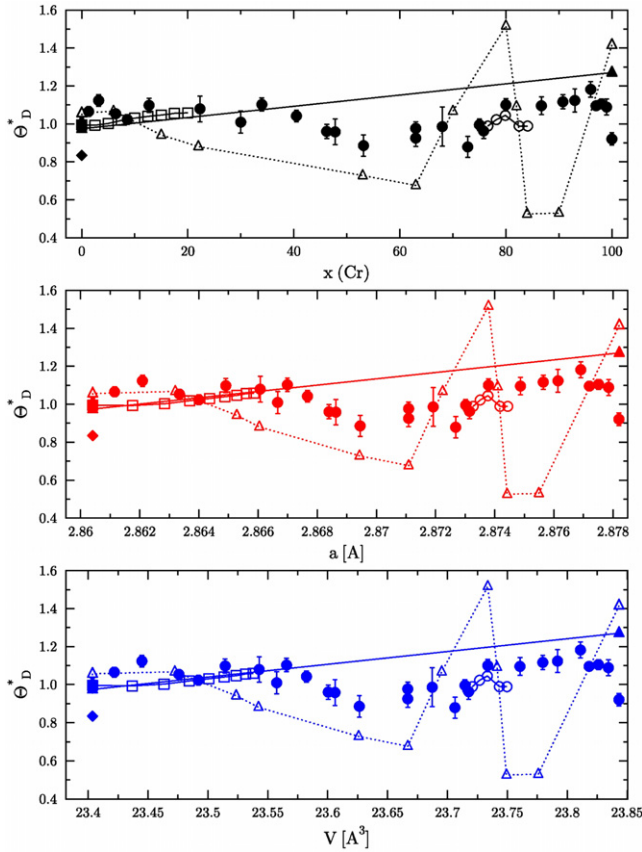


Figure 7. Normalized Debye temperature, Θ_D^* , versus the chromium concentration, x (top), the lattice constant, a , (middle) and the unit cell volume, V (bottom). Full circles represent the presently found data. For comparison, those obtained from the specific heat measurements are indicated by full triangles [9] and open circles [10], from the XRD experiment by full triangles [22], from the Lamb–Mössbauer factor by full diamonds [23] and from theoretical calculations by open squares [24]. The solid line shows the behaviour expected from Vegard’s law (for the XRD data), and the dotted one that found from the low temperature specific heat measurements [9].

they either decompose into Fe-rich and Cr-rich phases or, for higher temperatures, they change their structure into the sigma phase [26]. The increase of Θ_D^* observed in (B) probably reflects the hardening effect of chromium on the lattice dynamics, as its Debye temperature is higher than that of iron ($\Theta_D = 630$ K for chromium against 470 K for iron as determined from the heat capacity). The breakdown of this trend occurring at $x \approx 95$, which obviously reflects a softening of the dynamics, may be related to a decoupling of the Fe atoms from the underlying chromium lattice. It is very likely related to the spin-density waves that exist in the samples of Fe–Cr of these compositions [27]. The maximum drop of Θ_D^* happens for $x = 99.9$ and it reflects the weakest binding of Fe atoms to the chromium lattice. It can be expressed in terms of the harmonic force (spring) constant, γ . It must be stressed at this point that the value of Θ_D measured in this case, i.e. at Fe impurities dissolved in the chromium matrix, cannot be treated as the Debye temperature of the matrix, because in such cases the measured Θ_D reflects the dynamics of the impurity atoms embedded in a foreign lattice but not the dynamics of the lattice

itself. Consequently, it has, as a rule, different values to the Debye temperature of the host lattice itself, and, for this reason, it is termed as an effective Debye temperature, Θ_{eff} . On the other hand, its value can be used to determine the strength of bonding of the impurity atoms to the host lattice [28–31].

There are few relevant theoretical models available that can be used for this purpose [29, 32–34]. Following Visscher’s simple-impurity theory for a simple-cubic lattice [32], the quantity, Θ_{eff} , i.e. the effective Debye temperature as determined in the Mössbauer experiment (e.g. from equation (2)), is related to the Debye temperature of the matrix, Θ_D , by:

$$\Theta_{\text{eff}} = (M_{\text{Cr}}/M_{\text{Fe}})^{1/2}(\gamma_{\text{Fe-Cr}}/\gamma_{\text{Cr-Cr}})^{1/2}\Theta_D \quad (3)$$

where M_{Cr} and M_{Fe} are the masses of the host (Cr) and the impurity atom (Fe), while $\gamma_{\text{Fe-Cr}}$ and $\gamma_{\text{Cr-Cr}}$ are the spring constants of the impurity–host and the host–host binding. Θ_D is the Debye temperature of the host (Cr). Putting $\Theta_{\text{eff}} = 395$ K into this equation, one arrives at $\gamma_{\text{Fe-Cr}}/\gamma_{\text{Cr-Cr}} = 0.431$, which means that the coupling between Fe atoms and Cr atoms in this sample is by 57% weaker than the one between Cr atoms themselves. The reduction of the coupling is much greater if we take into account the fact that the value of $\Theta_{\text{eff}} = 395$ K is very likely overestimated due to an anharmonic behaviour of the dynamics of Fe atoms in the temperature interval of 145–300 K, as discussed in detail elsewhere [35, 36]. If one takes into account the value of $\Theta_{\text{eff}} = 292$ K, as determined for the harmonic mode, i.e. within the temperature range of 80–145 K, then one arrives at $\gamma_{\text{Fe-Cr}}/\gamma_{\text{Cr-Cr}} = 0.235$, indicating a 76.5% reduction in the spring constant value.

Gupta and Lal considered an atom undergoing an isotropic and harmonic motion, and they derived the following formula for γ [29]:

$$\gamma = \frac{Mk_B^2\Theta_D^2}{4\hbar^2} \quad (4)$$

that can be used to determine the absolute values of the spring constant itself if the Debye temperature is known. Using formula (4) for the present case, one obtains $\gamma_{\text{Fe-Cr}} = 64.8$ N m⁻¹ for $\Theta_{\text{eff}} = 395$ K, and 35.4 N m⁻¹ for $\Theta_{\text{eff}} = 292$ K. The corresponding value for $\gamma_{\text{Fe-Fe}} = 76.4$ N m⁻¹ and that for $\gamma_{\text{Cr-Cr}} = 164.8$ N m⁻¹.

Coming back to the data plotted in figure 7, it is obvious that our results do not confirm those found previously with the low temperature specific heat measurements [9]. Although there are some non-monotonous changes in the Debye temperature, as revealed in our study, their amplitude is not as high as reported previously, especially in the concentration range between ~80 and ~90 at.% Cr [9]. On the other hand, our results agree rather well with those deduced for $\sim 77 \leq x \leq \sim 84$ from the higher temperature specific heat measurements [10], as well as with those that have been recently calculated for Fe-rich alloys [24], although the latter do not show any enhancement for $x < 5$, as found with the present investigation.

4. Summary

The Debye temperature has been determined for disordered bcc-Fe_{100-x}Cr_x alloys in the whole compositional range from the centre shift of the Mössbauer spectra recorded in the temperature interval of 60–300 K. The data have been corrected for the lattice constant and the unit cell volume, but this procedure has not significantly changed the character of the behaviour, which has turned out to be non-monotonous. In the concentration ranges of (A) 0–~45 and (B) ~75–~95 the Debye temperature is enhanced relative to its value in metallic iron, while in the ranges (C) of ~45–~75 and (D) >95 the Debye temperature is reduced. The enhancement observed in (A) is correlated with the behaviour of the spin-waves stiffness constant, D_o , while the decrease observed in (D) correlates with the formation of the spin-density waves and can be interpreted as a decoupling of Fe atoms from the chromium lattice which itself shows anomalous dynamics [37, 38]. This effect seems to be, at least, in a qualitative accord with a softening effect of magnetism on the phonon spectrum that was observed for other systems [39]. On the other hand, the minimum in Θ_D observed for the near equiatomic composition coincides pretty well with the composition where the alloys are thermodynamically unstable and, upon heating, they either decompose into Fe- and Cr-rich phases or they change their crystallographic structure into the sigma phase.

Acknowledgment

The results presented in this paper were partly obtained in the frame of the bilateral Polish-Portuguese project 2007/2008.

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