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The Debye temperature of quasi-equi-atomic α -Fe–Cr alloys

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Abstract

A series of quasi-equi-atomic bcc Fe_{100-x}Cr_x alloys ($40.5 \leq x \leq 52.6$) was investigated with Mössbauer spectroscopy. The Debye temperature, Θ_D , was determined from the spectra measured in the temperature range of 30–300 K. It was revealed that the values of Θ_D found here increase linearly with x , but both the values and their rate of increase are slightly smaller than those recently found for σ -Fe–Cr alloys of similar composition. The small difference in Θ_D -value between the two phases do not reflect the huge crystallographic and mechanical differences between them.

1. Introduction

The Debye temperature, Θ_D , is a solid state scalar quantity that is, through the Debye model, related to all kinds of physical phenomena in which lattice vibrations are important. It is well known that for a given material the value of Θ_D depends on the method used to determine it, and, for a given method, on temperature, T . To illustrate the former, let us take the case of chromium, for which the room temperature value of $\Theta_D = 466$ K was found from the elastic constant data (Young modulus), and $\Theta_D = 580$ K was derived from the XRD data [1]. The influence of T on Θ_D can for example be presented for metallic bcc iron (α -phase), for which using the Mössbauer effect $\Theta_D = 400$ K was found from the data recorded in the temperature interval of 4–700 K, while $\Theta_D = 300$ K was determined for $700 \text{ K} \leq T \leq 1300 \text{ K}$ [2].

Consequently, a reasonable comparison of Θ_D -values found for different samples can only be made if the values were determined with the same method and in similar temperature conditions.

In our recent study Θ_D was, for the first time, determined for the σ -Fe_{100-x}Cr_x ($45 \leq x \leq 50$) alloys performing Mössbauer effect measurements in the temperature range of 4–300 K [3].

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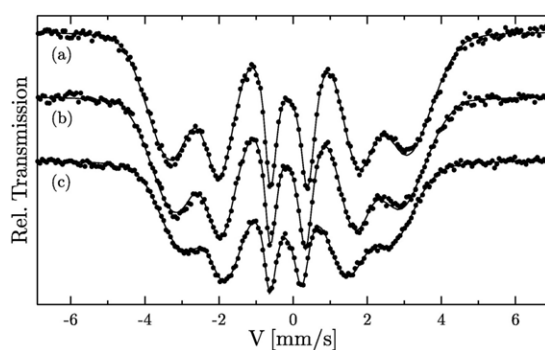


Figure 1. ^{57}Fe Mössbauer spectra recorded for the $\text{Fe}_{47.4}\text{Cr}_{52.6}$ sample at: (a) 60 K, (b) 166 K and (c) 299 K. The solid lines are the best fits to the experimental data.

The Debye temperature was found to increase linearly with x at the rate of 14.5 K/at.%, i.e. a relative increase of Cr content by $\sim 10\%$ caused a relative increase of Θ_{D} by $\sim 20\%$. The aim of the present investigation was to verify whether a similar behaviour shows the Debye temperature for α -Fe–Cr alloys of similar composition. A comparison of the data is of interest, as a possible difference can be entirely ascribed to the difference in crystallographic structure of the two series of samples. And the two structures are very different. The α -phase has the bcc structure with two atoms per unit cell and the atomic volume of $V_{\alpha} \approx 24 \text{ \AA}^3$ while the structure of the σ -phase is tetragonal and the unit cell, having the volume of $V_{\sigma} \approx 353 \text{ \AA}^3$, hosts 30 atoms distributed over five different crystallographic sites. The difference in crystal structure is reflected in the fact that many physical properties of the two phases are dissimilar, the difference sometimes being dramatic. In particular, magnetic properties of the σ -FeCr alloys are almost one order of magnitude weaker than those of the α -FeCr alloys [4], while mechanical properties of the sigma phase such as brittleness and hardness are by factor of 3–4 greater than those of the alpha phase.

2. Experimental details

A series of α - $\text{Fe}_{100-x}\text{Cr}_x$ alloys, with $x = 40.5, 46.2$ and 52.6 , were prepared by melting appropriate quantities of Fe (99.95% purity) and Cr (99.5% purity) in an arc furnace under argon atmosphere. The ingots obtained were next solution treated in vacuum at 1273 K for 72 h, and this was followed by a quenching into ice water. Another sample with $x = 47.8$ was fabricated by mechanical milling as described elsewhere [3]. It had a nanocrystalline structure with the average size of grains equal to 7.4 nm, but the grains were in the form of aggregates having the average size of 30 μm . All the samples obtained were found to be 100% in the α -phase as determined by Mössbauer spectroscopy (MS) and x-ray diffraction (XRD) measurements performed at room temperature. The chemical composition was determined by a microprobe analysis.

^{57}Fe Mössbauer spectra were recorded in a transmission geometry for samples in the form of powder that was obtained by filing the ingots with a diamond file. The samples were maintained in a closed-cycle helium cryostat that enabled temperature control with an accuracy of ± 0.3 K in the range of 30–300 K. The $^{57}\text{Co}/\text{Rh}$ source of the gamma rays was moved with a constant acceleration, and the velocity was calibrated with an α -Fe foil kept at 295 K. Examples of the spectra are shown in figure 1.

3. Results and discussion

The spectra were analysed in terms of the standard hyperfine (hf) field distribution (HFD) method. Following previous experimental results, it was assumed in the fitting procedure that the hf field was linearly correlated with the centre shift, CS [5]. In addition, it was assumed that the ratio of the lines in each spectrum was equal to 3:2:1. Interpretation of the temperature dependence of CS is not easy. In general, CS can be written as a sum of two terms:

$$CS = IS + SOD \quad (1)$$

where IS is the isomer shift and SOD is due to the second-order Doppler shift. *A priori*, both terms can be temperature dependent. According to theoretical calculations IS(T) is a complex function as several factors may contribute to it, in particular the lattice expansion [6]. Consequently, there is no simple way known for separating the two terms. The authors of [7] did such separation by subtracting the calculated SOD term from the measured CS(T), showing that, in fact, IS is weakly temperature dependent. However, their procedure cannot be applied in general, as it needs the knowledge of the exact value of the Debye temperature, Θ_D . It can be rather treated as a reminder that the values of Θ_D obtained assuming that the total temperature dependence of the centre shift goes via the SOD term may be biased. On the other hand, as is well known, Θ_D -values strongly depend on the method used to determine them, so it is hoped that the bias introduced by this simplification is smaller than the difference in the Θ_D -values obtained by different methods. The second term, which is related to the atomic mean square displacement in the lattice, is hence strongly temperature dependent, and can be easily calculated. This is the main reason why practically in determination of the Debye temperature from the centre shift the total temperature dependence of CS is ascribed to the SOD term [8–12]. In these circumstances the use of the simplified procedure seems to be justified, all the more so since the concept of the underlying Debye model itself is simplistic and the Θ_D -values obtained agree, in general, with those found with other techniques.

Neglecting then the temperature dependence of the first term, the temperature dependence of the average CS, $\langle CS(T) \rangle$, can be, in the approximation of the Debye model, expressed as follows:

$$\langle CS \rangle(T) = -\frac{3kT}{2mc} \left(\frac{3\theta_D}{8T} + 3 \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^3}{e^x - 1} dx \right) \quad (2)$$

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

In figure 2 a typical $\langle CS(T) \rangle$ dependence is shown with the solid line representing the best fit to experimental data.

The Θ_D -values obtained for the samples studied, by fitting equation (2) to experimental data, are presented as full symbols in figure 3. For comparison, those found previously with the same procedure for the σ -phase series are plotted, too [3]. Although particular values of Θ_D may be biased with some systematic error having its source in the method used, the trend found versus composition for a given set of samples (phases) should be correct. It can be seen that the data for the α -series, both for the bulk samples and for the nanocrystalline ones, have slightly lower values (by $\sim 5\%$). Also their increase with x is $\sim 15\%$ smaller (12.5 K/at.% instead of 14.5 K/at.%). In general, the Debye temperature is high for hard materials and low for soft ones. This is not the case here: a small difference between the two sets of Θ_D -values reflects neither a huge difference between the brittleness and hardness of the two phases (the σ -phase is by a factor of 3–4 harder than the α -phase [13]) nor a pronounced difference in elastic properties (the Young modulus of the α -phase is at RT almost twice larger than that of the σ -phase, while at 1023 K it is $\sim 20\%$ smaller [14]).

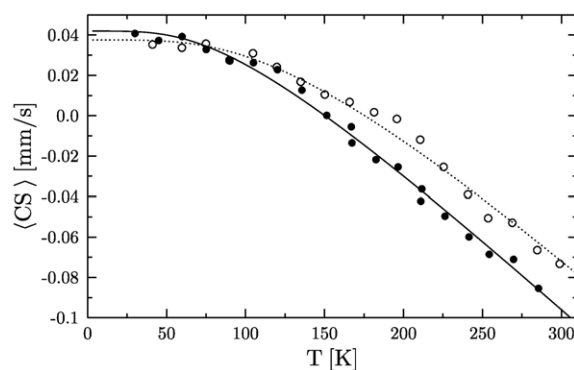


Figure 2. Average centre shift, $\langle CS \rangle$, versus temperature, T , for $Fe_{59.5}Cr_{40.5}$ (full symbols) and $Fe_{47.4}Cr_{52.6}$ samples (open symbols). The lines represent the best fit to the data in terms of equation (2).

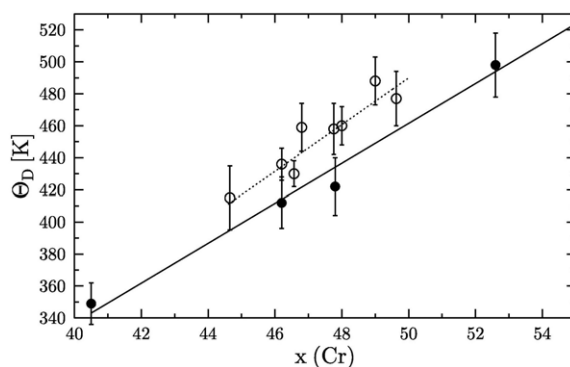


Figure 3. The Debye temperature, Θ_D , versus Cr content, x for the $\sigma-Fe_{100-x}Cr_x$ alloys (open symbols) and for the $\alpha-Fe_{100-x}Cr_x$ alloys (full symbols). The lines stand for the best linear fits to the data.

The differences between the Θ_D -values shown in figure 3 for the σ - and α -phases could possibly be explained in terms of their structural properties. Towards this end let us consider the following three factors: (a) number of bonds, n ; (b) length of bonds, d ; and (c) average volume per atom per unit cell, v . As regards (a), $n = 13.5$ for the σ -phase and $n = 8$ for the α -phase. It is clear that Θ_D is not simply correlated with n . Taking the nearest-neighbour distance for d one arrives at $\langle d \rangle = 2.61 \text{ \AA}$, on average, for the σ -phase, and $d = 2.49 \text{ \AA}$ for the α -phase. By intuition, Θ_D should be greater for shorter d , just opposite to what is found in this study. Finally, considering the third factor, i.e. the average volume per atom per unit cell, one arrives at $v = 11.8 \text{ \AA}^3$ for the σ form and $v = 11.9 \text{ \AA}^3$ for the α form. The tiny difference of $\sim 1\%$ in v cannot explain the difference in Θ_D either. In other words, it seems there is no simple explanation of the difference in Θ_D for the phases studied, in terms of the above considered structural features.

The second effect observed, i.e. the increase of Θ_D with x , can be qualitatively understood in terms of the hardening effect of chromium. Its Debye temperature is significantly greater than that of iron, so its increase in the sample should enhance Θ_D , provided structural parameters of the sample are undisturbed by the addition of chromium (which is the case here).

Theoretical calculations and/or measurements of complete phonon spectra for the two phases are therefore necessary in order to explain their dynamical properties and the small difference in Θ_D -value between the two phases.

4. Conclusions

The results obtained in this investigation permit the following conclusions to be drawn:

- (1) The Debye temperature, Θ_D , of quasi-equi-atomic α -Fe–Cr alloys grows linearly with the Cr content, x , at the rate of 12.5 K/at. %.
- (2) Both the values of Θ_D and the rate of its increase with x are slightly smaller than the corresponding values for the σ -Fe–Cr alloys.
- (3) The difference between the Θ_D -values for the α - and σ -phases in quasi-equi-atomic Fe–Cr alloys cannot be simply explained in terms of such structural parameters as number and length of bonds, and the average volume per atom per unit cell.

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