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2004 J. Phys.: Condens. Matter 16 L343

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LETTER TO THE EDITOR

The Debye temperature of a nanocrystalline σ -Fe_{55.4}Cr_{44.6} alloy

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Received 11 May 2004

Published 9 July 2004

Online at stacks.iop.org/JPhysCM/16/L343

doi:10.1088/0953-8984/16/29/L01

Abstract

The Debye temperature $\Theta_D = 411 \pm 12$ K was determined for a σ -Fe_{55.4}Cr_{44.6} alloy, with average grain size of 27 nm, from Mössbauer spectra recorded in the temperature range of 4–300 K. The result fits well with those found previously for samples of different Cr content, x , with mean grain sizes in the micrometre range. Θ_D was found to increase linearly with x at the rate of 14.6 K/at. %.

1. Introduction

Many physical properties of nanoscale materials differ from the corresponding bulk ones. Dynamical properties are not exceptional in this respect, which can be evidenced by the Debye temperature, Θ_D , found for various nanoscale systems. A deviation from the bulk value of the nanoparticle's Θ_D reflects strong influences of the surface-atomic arrangement. Free and loosely embedded fine particles show a decrease of Θ_D , while for well-embedded metallic particles, such as the ones prepared by ion implantation, Θ_D seems to depend on the host matrix; if the matrix is harder than the particles, then Θ_D of the latter is enhanced, e.g. Sn particles in an Si matrix [1], and vice versa, e.g. Co particles in an Ag matrix [2]. For free or loosely embedded particles, the observed increase of Θ_D with particle size points to a decrease of the surface-induced effects. In fact, Harada and Ohshima [3] showed that in the case of small Au clusters Θ_D (surface) = 97 K against Θ_D (core) = 165 K, the latter being close to the bulk value of 168 K. The role of the surface in the dynamical properties was also demonstrated by showing that Θ_D grows with film thickness [4] as well as that the value of Θ_D measured in plane is larger than the one measured out of plane [4, 5].

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In this paper the determination of Θ_D for a sample of σ -Fe_{55.35}Cr_{44.65} alloy with mean grain size in the nanometre range by means of Mössbauer spectroscopy (MS) is presented and compared with corresponding results obtained recently for samples with grain size in the micrometre range [6].

2. Experimental details

The nanocrystalline sample was prepared by mechanical alloying using a planetary mill (Fritsch P-7) at a disc rotating speed of 640 rpm, equipped with hardened steel vials and balls (seven pieces) with mixtures of powders of Fe (99.9% purity, grain size $<40 \mu\text{m}$) and Cr (99.2% purity, grain size $\sim 100 \mu\text{m}$) in argon atmosphere. The weight of the sample powder was 5 g and the powder-to-ball weight ratio was 1/20. The total milling time was 16 h, interrupted for 15 min every hour. The composition of the sample was determined by microprobe analysis and the result gave Fe_{55.4}Cr_{44.6}. The sample as obtained was found to be in the α -phase as determined by MS and x-ray diffraction (XRD) measurements. Transformation into the σ -phase was performed by isothermal annealing in vacuum at 973 K for 5 h. When the annealing was completed, the cooling down was performed in a flow of helium gas cooled at liquid nitrogen temperature. The phase purity was checked both by MS and by XRD measurements.

The XRD technique using Cu K α radiation ($\lambda = 0.154184 \text{ nm}$) at room temperature was also used to determine the mean crystallite sizes and micro-strains, obtained from the width of XRD peaks using the Williamson–Hall method [7]. The results gave 10 nm and 0.60% (α -phase) and 27 nm and 0.21% (σ -phase) for mean crystallite sizes and micro-strains, respectively.

⁵⁷Fe Mössbauer spectra were recorded in transmission geometry using a standard spectrometer and a ⁵⁷Co/Rh source for the 14.4 keV gamma rays. The sample was mounted in a cryostat that enabled keeping a constant temperature with an accuracy better than $\pm 0.2 \text{ K}$ within a 1–2 day run needed to record a spectrum of good statistical quality.

3. Results

The value of Θ_D can be determined by means of MS from the temperature dependence of the isomer shift, IS(T):

$$\text{IS}(T) = \text{IS}_0(T) + \text{IS}_{\text{SODS}}(T) \quad (1)$$

where $\text{IS}_0(T)$ represents the T -dependence of the charge density at the probe nucleus (which is generally weak). The second term, IS_{SODS} , is the so-called second-order Doppler shift, which, using the Debye model for the phonon spectrum, can be described by

$$\text{IS}_{\text{SODS}}(T) = -\frac{3kT}{2mc} \left[\frac{3\Theta_D}{8T} + 3 \left(\frac{T}{\Theta_D} \right)^3 \int_0^\tau \frac{x^3}{e^x - 1} dx \right] \quad (2)$$

where m is the mass of the ⁵⁷Fe nucleus, k Boltzmann's constant, c the velocity of light, and $\tau = \Theta_D/T$ the reduced temperature.

The spectra (examples are displayed in figure 1) were analysed using a least-squares iteration procedure. The σ -phase has five different crystallographic sites, which can be occupied by Fe and Cr atoms. For that reason each recorded spectrum was assumed to consist of a superposition of five subspectra characterized by different hyperfine parameters (hyperfine field, B , quadrupole splitting, QS, and isomer shift, IS). In the spectra measured at temperatures lower than the Curie point, T_C , hyperfine fields or their distributions should be observed for all crystallographic sites. In the fitting procedure the relative intensity of each subspectrum

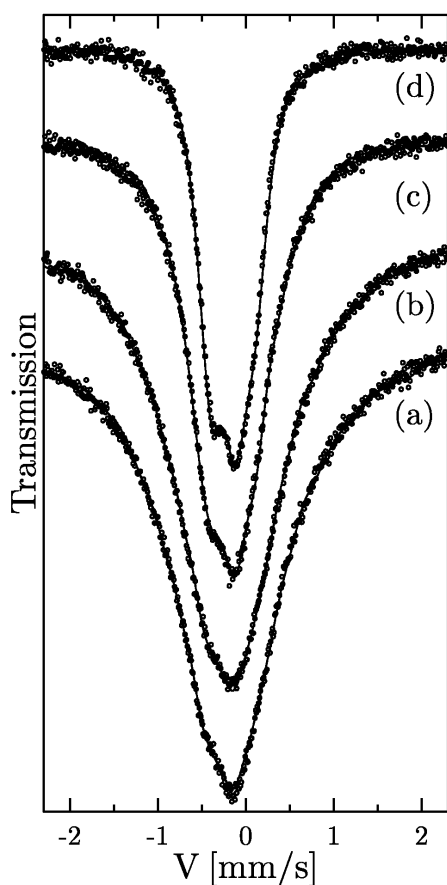


Figure 1. ^{57}Fe Mössbauer spectra recorded on the nanocrystalline $\sigma\text{-Fe}_{55.35}\text{Cr}_{44.65}$ alloy at (a) 4.2 K, (b) 20 K, (c) 40 K and (d) 60 K.

and the values of QS were assumed to be temperature independent. All spectra were fitted simultaneously with the above restriction. The mean isomer shift, $\langle\text{IS}\rangle$, with a typical error $\pm 0.02\text{--}0.03\text{ mm s}^{-1}$, was calculated as the weighted one over all subspectra.

A value of $\Theta_{\text{D}} = 411 \pm 12\text{ K}$ was derived by fitting equation (2) to the temperature dependence of the mean isomer shift. Figure 2 shows that T -dependence of $\langle\text{IS}\rangle$ as well as the best fit. A comparison of this Θ_{D} -value with those determined recently for samples with grain sizes in the micrometre range of $\sigma\text{-FeCr}$ [6] is made in figure 3. The Θ_{D} -value obtained for the nanocrystalline sample fits well with those found for the microcrystalline ones with a linear increase of Θ_{D} at a rate of $14.6\text{ K/at.}\%$. This behaviour is consistent, at least qualitatively, with the difference in Θ_{D} found for ^{57}Fe embedded in either an Fe or a Cr matrix [8, 9].

The agreement of the presently found value of Θ_{D} with those characteristic of bulk samples seems to be reasonable in light of the dependence of Θ_{D} on grain size as known from literature for other systems [2, 4]. In addition, our nanoscale sample, as revealed by an SEM study [10], exists in the form of agglomerates with mean diameter of $\sim 30\ \mu\text{m}$. This means that one agglomerate consists, on average, of $\sim 10^9$ particles. In these circumstances our nanocrystalline particles cannot be regarded as free ones but rather as embedded in a matrix formed by the same particles. Consequently, the dynamics of the lattice seems to be determined by these agglomerates, and the measured Debye temperature agrees with that characteristic of the microscale samples.

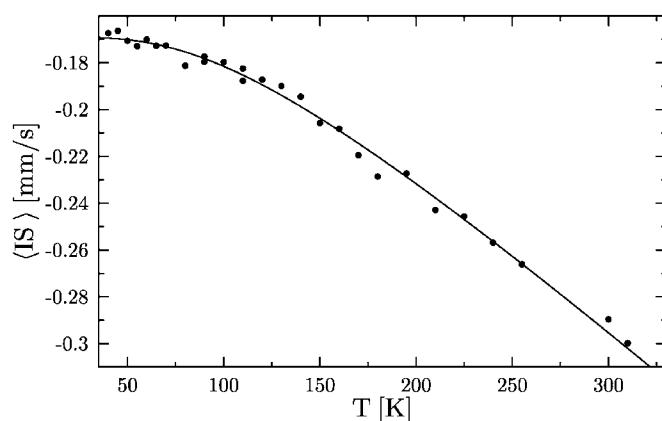


Figure 2. Average isomer shift, $\langle IS \rangle$, versus temperature, T . The solid curve represents the best fit to the data in terms of equation (2).

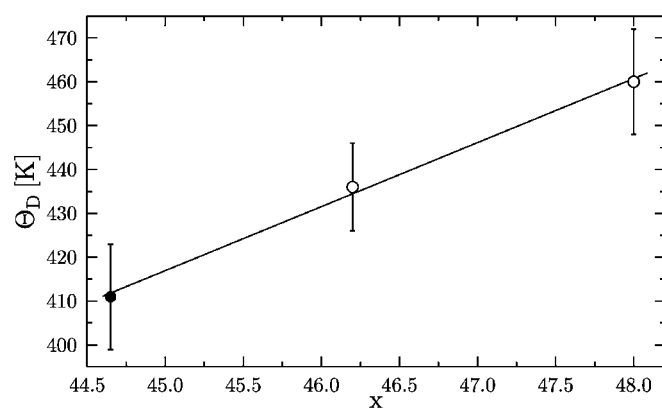


Figure 3. Debye temperature, Θ_D , versus Cr-content, x for σ -Fe $_{100-x}$ Cr $_x$ alloys. (●) stands for the sample with grain size in the nanometre range and (○) for those with grain size in the micrometre range. The solid line represents the best fit to the data.

4. Conclusions

The following conclusions can be drawn based from the present study:

- The Debye temperature of the investigated nanocrystalline sample $\Theta_D = 411 \pm 12$ K fits well with those found previously for microcrystalline samples.
- Θ_D of σ -FeCr alloys increases linearly with Cr content at the rate of 14.6 K/at.%, reflecting the hardening effect of chromium.

This work was supported in part by Austro-Polish project (16/01).

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