

Determination of the Debye temperature of the σ -phase Fe-Cr alloys

J. Cieřlak, S. M. Dubiel,* and J. Żukrowski

Faculty of Physics and Nuclear Techniques, The University of Mining and Metallurgy (AGH), al. Mickiewicza 30, PL-30-059 Kraków, Poland

M. Reissner and W. Steiner

Institute of Applied and Technical Physics, Vienna University of Technology, Wiedner Hauptstrasse 8-10, A-1040 Wien, Austria

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^{57}Fe Mössbauer spectra were recorded on the σ -phase samples of $\text{Fe}_{54}\text{Cr}_{46}$, $\text{Fe}_{52}\text{Cr}_{48}$, and $(\text{Fe}_{54}\text{Cr}_{46})\text{-}0.3$ at % Ti alloys in the temperature range of $40 \text{ K} \leq T \leq 330 \text{ K}$. From the temperature dependence of the average isomer shift the Debye temperature Θ_D was evaluated as equal to 437(7) K, 460(12) K, and 471(22) K for the three samples, respectively.

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I. INTRODUCTION

The σ phase was discovered in 1923 in an Fe-Cr alloy,¹ and its crystal structure was identified only in 1954 also in the Fe-Cr system.² Nowadays, 42 examples of binary-alloy systems are known in which it exists.³ Particular interest in the σ -Fe-Cr system stems not only from the fact it represents the archetype of the phase, but mainly because the system is of particular interest both for scientific and technological reasons. The σ phase itself is of interest due to its complex close-packed tetragonal (tcp) structure with 30 atoms distributed over five nonequivalent sites in a unit cell. The space group is $D_{4h}^{14}-P4_2/mnm$. Its physical properties are substantially different from those characteristic of the α phase (bcc), from which it precipitates either as a result of isothermal annealing of quasiequiatomic alloys in the temperature interval⁴ of $\sim 800 \text{ K} \leq T \leq \sim 1100 \text{ K}$ or by mechanical alloying.⁵ Its most striking feature is brittleness and hardness, the latter by a factor of 4–5 larger than that of the α phase. The σ -Fe-Cr is weakly ferromagnetic, i.e., its Curie temperature and the magnetic moment per Fe atom are one order of magnitude smaller than those of α -Fe-Cr of the same chemical composition.⁶

In view of these and other differences in the physical properties between α and σ , it seems interesting to know the Debye temperature of the latter, all the more so, it is, to our best knowledge, unknown so far.

One of the experimental methods that can be used for that purpose is the Mössbauer spectroscopy. The Debye temperature Θ_D can be determined by means of this method from the temperature dependence of the isomer shift IS

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

where IS_0 is a term representing the dependence of IS on the charge density at the probe nucleus and has only a weak temperature dependence.⁷ The second term in Eq. (1), IS_{SODS} , is the so-called second-order Doppler shift. Assuming the whole dependence of IS on T originates from the second term, and using the Debye model for the phonon spectrum one can write the following formula

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

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

II. EXPERIMENT

Samples of $\text{Fe}_{54}\text{Cr}_{46}$, $\text{Fe}_{52}\text{Cr}_{48}$, and $(\text{Fe}_{54}\text{Cr}_{46})\text{-}0.3$ at % Ti alloys were prepared by melting appropriate amounts of Fe (99.95% purity), Cr (99.5% purity), and Ti (99.9% purity) in a vacuum induction furnace. The ingots received were cut into cubes of 5 mm size, which were next solution treated in vacuum of the order of 10^{-3} Pa for 24 h at 1473 K followed by water quenching. The chemical composition was determined on the homogenized samples by an electron probe microanalysis. The samples were next rolled down to a final thickness of $\sim 30 \mu\text{m}$ and then vacuum annealed at 1173 K for 1 h to remove strain. Their transformation into the σ phase was made by an isothermal annealing at 973 K. The verification of the transformation process was done both by recording the Mössbauer spectra as well as the x-ray diffractograms.⁸

^{57}Fe Mössbauer spectra were recorded in transmission geometry using a standard spectrometer and a $^{57}\text{Co}/\text{Rh}$ source for the 14.4-keV γ rays at temperatures between 40 and 330 K. The temperature of the samples, which were placed in a continuous-flow cryostat, was constant within 0.1 K during the 1-day run needed to record a spectrum of a good statistical quality.

III. RESULTS

A. Spectra analysis

The spectra, whose selected examples are shown in Fig. 1, were analyzed in two ways, using a least-squares iteration procedure. As the only spectral parameter relevant to the determination of the Debye temperature is the average isomer shift (the center of gravity of the spectrum) and its value does not depend on the value of the quadrupole splitting, the latter parameter was neglected. In the first way (I), the spectra were fitted in terms of the distribution of the isomer shift.

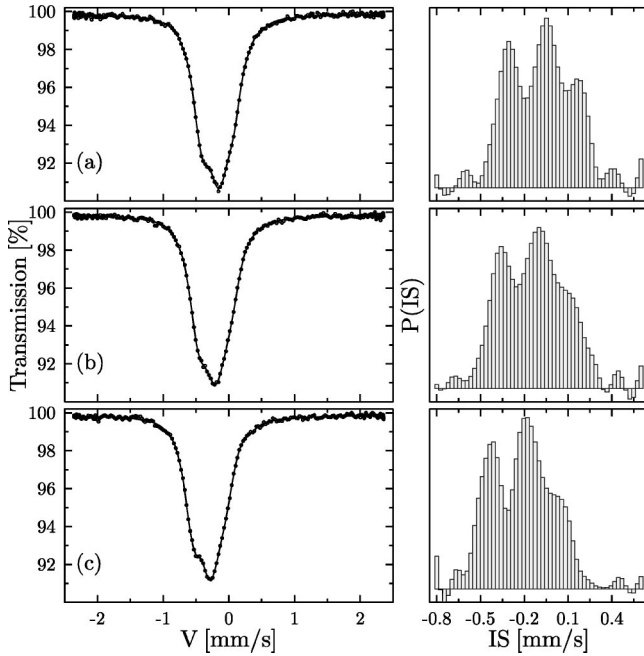


FIG. 1. ^{57}Fe Mössbauer spectra recorded on the sample of $\text{Fe}_{54}\text{Cr}_{46}$ alloy at (a) $T=80$ K, (b) $T=200$ K, and (c) $T=320$ K, and the corresponding distributions of the isomer shift (right-hand side).

Those obtained for the spectra shown in Fig. 1, are presented alongside on the right-hand side of the figure. The average isomer shift, $\langle \text{IS} \rangle$, was determined by integrating the distribution, i.e., $\langle \text{IS} \rangle_{\text{I}} = \int \text{IS} P(\text{IS}) d\text{IS} / \int P(\text{IS}) d\text{IS}$. For the temperature regime where the samples are paramagnetic, this way of spectra analysis can be regarded as a model-free one. In the second way (II), the spectra were analyzed assuming they were a superposition of a number of single-line subspectra, each corresponding to one site occupied by the probe Fe atoms. The number of the sites occupied by Fe atoms is still an open question. According to experimental results based on x-ray diffraction measurements, Fe atoms reside on all five sites,^{2,9} while according to recent theoretical calculations, only three sites are occupied by Fe atoms.^{10–12} In view of this unclear situation, our spectra were fitted assuming they were composed of 3, 4, or 5 single-line subspectra having the same linewidth, Γ , which was, however, treated as a fit parameter. It has turned out that the spectra can be well fitted independently of the number of the subspectra. The only difference was the value of Γ , which was equal to 0.34–0.35 mm/s in the case of three subspectra, to 0.31–0.32 mm/s in the case of four subspectra, and to 0.28–0.30 mm/s in the case of five subspectra. The values of $\langle \text{IS} \rangle_{\text{II}}$, the essential quantity to determine Θ_D , were practically independent of the number of subspectra, and were in a good agreement with the corresponding values obtained in the first way of spectra analysis, $\langle \text{IS} \rangle_{\text{I}}$. An example of the data found for the spectra recorded on the sample of $\text{Fe}_{54}\text{Cr}_{46}$ is given in Table I.

B. Determination of the Debye temperature

The temperature dependence of the average isomer shift, $\langle \text{IS} \rangle = (\langle \text{IS} \rangle_{\text{I}} + \langle \text{IS} \rangle_{\text{II}}) / 2$, was used to determine the De-

TABLE I. Average values of the isomer shift (relative to $\alpha\text{-Fe}$) as calculated from method I, $\langle \text{IS} \rangle_{\text{I}}$ and method II, $\langle \text{IS} \rangle_{\text{II}}$ for the sample of $\text{Fe}_{54}\text{Cr}_{46}$.

	$T=80$ K	$T=200$ K	$T=320$ K
$\langle \text{IS} \rangle_{\text{I}}$ (mm/s)	-0.07	-0.13	-0.21
$\langle \text{IS} \rangle_{\text{II}}$ (mm/s)	-0.08(2)	-0.13(2)	-0.21(2)

bye temperature. The data presented in Fig. 2 for the three samples investigated, was fitted using Eq. (2), yielding the following values of Θ_D : 437(7) K for $\text{Fe}_{54}\text{Cr}_{46}$, 460(12) K for $\text{Fe}_{52}\text{Cr}_{48}$, and 471(22) K for $(\text{Fe}_{54}\text{Cr}_{46})\text{-0.3 at\% Ti}$. To our best knowledge, this is the first determination of the Debye temperature for the σ phase in general, and for the $\sigma\text{-Fe-Cr}$, in particular. From the data it follows that the Debye temperature, like other physical properties of the σ phase, depends on its chemical composition. In particular, Θ_D increases with Cr content. Such behavior may be expected as the Debye temperature of chromium is significantly larger than that of iron. For example, $\Theta_D = 331(12)$ K for ^{57}Fe atoms in iron¹³ against $\Theta_D = 445(15)$ K for ^{57}Fe atoms in Cr-rich (α') Cr-Fe phase.¹⁴ The comparison of the Debye temperature should be made between the values obtained with the same method and for the same temperature range, as it is known that the value of Θ_D depends on the used method.¹⁵ In the light of a lack of data, one cannot compare the present data with that characteristic of $\alpha\text{-Fe-Cr}$ with similar composition. If one, however, assumes for $\alpha\text{-Fe-Cr}$ that Θ_D scales linearly with the composition, than taking into account the data of Ref. 10, one gets $\Theta_D \sim 400$ K for a quasiequiatomic $\alpha\text{-Fe-Cr}$ alloy.

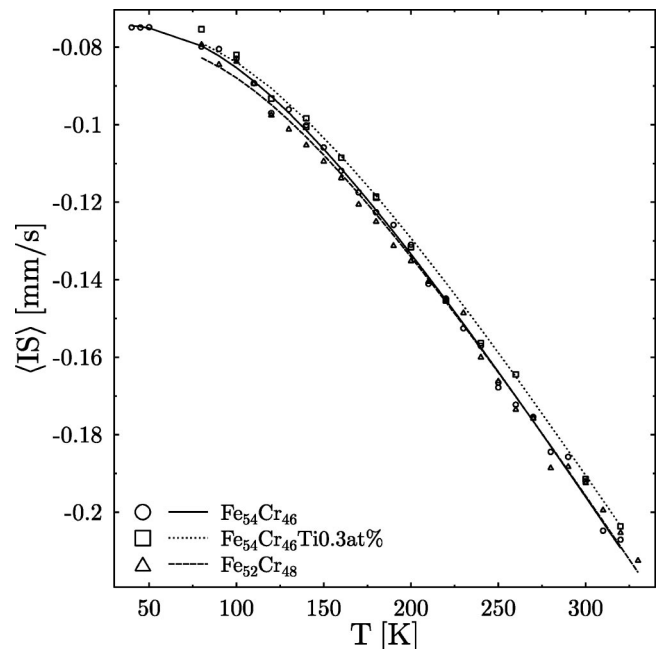


FIG. 2. The average isomer shift $\langle \text{IS} \rangle$ versus temperature T for the samples investigated. The lines stand for the bestfits to the data using Eq. (2).

This is $\sim 10\%$ less than the value found in a present study for the σ -Fe-Cr. The $\sim 10\%$ enhancement of the Debye temperature found for the σ phase agrees well with the corresponding enhancement of the Lamb-Mössbauer (recoilless fraction) factor revealed recently for the investigated samples.^{16,17}

IV. SUMMARY

The Debye temperature of the σ -Fe-Cr alloys has been determined from the second-order Doppler shift. The values

of Θ_D found span over the range of $437 \text{ K} \leq \Theta_D \leq 471 \text{ K}$, depending on the alloy composition. These values are by $\sim 10\%$ larger than the estimated value of Θ_D for the α -Fe-Cr alloy of similar composition. Such relationship agrees well with the corresponding relationship between the recoilless fractions of the two phases.

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*Corresponding author. FAX: 4812 634 0010.

Email address: dubiel@novell.ftj.agh.edu.pl

¹E.C. Bain, *Chem. Met. Eng.* **28**, 23 (1923).

²G. Bergman and D.P. Shoemaker, *Acta Crystallogr.* **7**, 857 (1954).

³E.O. Hall and S.H. Algie, *Metall. Rev.* **11**, 61 (1966).

⁴T. B. Massalski, *Binary Alloy Phase Diagrams*, (ASM International, Metals Park, OH, 1990), Vol. 1.

⁵F.O. Costa, G. Le Caër, and N.A. de Campos, *Phys. Status Solidi A* **183**, 235 (2001).

⁶Y. Sumimoto, T. Morija, H. Ino, and F.E. Fujita, *J. Phys. Soc. Jpn.* **35**, 461 (1973).

⁷S. Willgeroth, H. Ullrich, and J. Hesse, *J. Phys. F: Met. Phys.* **14**, 387 (1984).

⁸J. Cieślak, S.M. Dubiel, S. Środa, and Z. Żurek, *J. Alloys Compd.* **333**, 190 (2002).

⁹H.L. Yakiel, *Acta Crystallogr., Sect. B: Struct. Sci.* **39**, 20 (1983).

¹⁰J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, and C. Fiolhais, *Phys. Rev. B* **46**, 6671 (1992).

¹¹M. Sluiter, K. Esfariani, and Y. Kawazoe, *Phys. Rev. Lett.* **75**, 3142 (1995).

¹²J. Havrankova, J. Vřešťal, L.G. Wang, and M. Šob, *Phys. Rev. B* **63**, 174104 (2001).

¹³P. Debruner and R.J. Morrison, *Rev. Mod. Phys.* **4**, 63 (1964).

¹⁴H. Kuwano and Y. Morooka, *J. Jpn. Inst. Met.* **45**, 457 (1981).

¹⁵R.H. Wilson, E.F. Skeleton, and J.L. Katz, *Acta Crystallogr.* **21**, 635 (1966).

¹⁶J. Cieślak, S.M. Dubiel, and B. Sepiol, *Solid State Commun.* **111**, 613 (1999).

¹⁷A. Blachowski, J. Cieślak, S.M. Dubiel, and B. Sepiol, *Intermetallics* **8**, 963 (2000).