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A Study of Thermodynamic Properties of Dilute Fe–Pd Alloys by the ^{57}Fe Mössbauer Spectroscopy

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Room-temperature Mössbauer spectra of ^{57}Fe were recorded for iron-based solid solutions $Fe_{1-x}Pd_x$ with x in the range $0.010 \leq x \leq 0.066$. The obtained data were analysed in terms of the binding energy E_b between two palladium atoms in the studied materials using the extended Hrynkiewicz–Królas idea. It was found that the energy is positive, which indicates that Pd atoms interact repulsively. The extrapolated value of E_b for $x = 0$ was used to compute the enthalpy of solution $H_{\text{Fe-Pd}}$ of palladium in iron. It turned out that the value of $H_{\text{Fe-Pd}}$ determined on the basis of the ^{57}Fe Mössbauer spectra is in qualitative agreement with the corresponding value derived from Miedema's model of alloys and is at variance with the available calorimetric data for the Fe–Pd system.

topics: Mössbauer spectroscopy, enthalpy of solution, iron alloys

1. Introduction

The ^{57}Fe Mössbauer spectroscopy constitutes a valuable tool for the investigation of impurity atoms dissolved in iron [1–3]. The technique is especially effective when impurity atoms surrounding the Mössbauer probe induce a sufficiently large change in the hyperfine field at the probe nucleus, resulting in clearly resolved components in the spectrum that correspond to distinct configurations of neighbouring atoms. As demonstrated in our recent papers [4–8], this technique can also be effectively applied to binary Fe systems where the influence of impurities on the hyperfine field at the ^{57}Fe nucleus is weak. These observations are noteworthy because the interactions between impurities and the host lattice are directly linked to the enthalpy of solution of impurity atoms in iron [9]. This enthalpy is a key parameter widely used in formulating and testing theoretical models of binary alloys, as well as in computational approaches to alloy design [10–13]. Additionally, in certain instances, Mössbauer spectroscopy can serve as a valuable complement to calorimetric measurements when evaluating the enthalpy values [14]. This approach is, however, limited by the fact that calorimetric experiments are performed at relatively high temperatures, where the γ phase, characterized by a face-centred cubic (fcc) structure, is stable for most iron-based systems, whereas Mössbauer spectroscopy probes the enthalpy of solution in the low-temperature α phase, characterized by a body-centred cubic (bcc) structure. The above considerations prompted us to use ^{57}Fe Mössbauer spectroscopy as a means of providing experimental enthalpy of solution data for various elements in $\alpha-$iron systems.

In the present work, transmission ^{57}Fe Mössbauer spectroscopy was applied to dilute binary Fe–Pd alloys in order to extend the knowledge of the thermodynamic properties of this system in the solid state, namely, the binding energy of two palladium atoms and the enthalpy of solution $H_{\text{Fe-Pd}}$ of Pd in the α-Fe matrix. Palladium was selected due to its complete miscibility with iron, its significant influence on the local magnetic and electronic structure of the host, and the expectation that it would act as a non-magnetic impurity, which may locally disturb ferromagnetic ordering and affect atomic pair formation. These effects are of particular importance for thermodynamic modelling and the interpretation of hyperfine interactions.

To the best of our knowledge, no calorimetric data on the enthalpy of solution of palladium in the low-temperature α-phase of iron have been reported. This motivated us to apply ^{57}Fe Mössbauer spectroscopy to determine the thermodynamic parameters for dilute Fe–Pd alloys at about 700 K, where atomic diffusion is effectively frozen and the system remains in the α-Fe phase.

2. Experimental details and results

2.1. Measurements and data analysis

The room-temperature Mössbauer spectra of ^{57}Fe were measured for iron-based solid solutions $Fe_{1-x}Pd_x$ with x in the range $0.0095 \leq x \leq 0.0663$. The samples of disordered $Fe_{1-x}Pd_x$ alloys were obtained at the Institute of Physics of the Pedagogical University of Kraków. The composition and homogeneity of each sample were checked using energy-dispersive X-ray spectroscopy (EDS) with the help of an electron micro-probe. More information on this can be found in [15]. The spherical ingots were cold-rolled to a final thickness of $\approx$ 0.02 mm. The room-temperature ^{57}Fe Mössbauer spectra were then recorded for the resulting foils using a constant-acceleration POLON Warszawa company Mössbauer spectrometer of standard design. The spectrometer velocity scale was calibrated using a spectrally pure, thermally annealed α-Fe metallic foil with a thickness of 25 μm, in accordance with the commonly adopted calibration procedure. Subsequently, the samples were annealed in vacuum at 1270 K for 2 h, after which they were slowly cooled to room temperature over a period of 6 h. Under these conditions, diffusion effectively ceases at about 700 K [16], and thus the observed atomic distributions in the annealed specimens should correspond to a frozen-in state characteristic of 700 K. The spectra obtained for these samples are shown in Fig. 1.

All spectral analyses were carried out using the MOS software, authored by Jan Żukrowski. The program enables least-squares fitting of spectral components in the form of single lines, quadrupole doublets, or magnetic sextets, depending on the spectrum type. The measured spectra were fitted using six-line subspectra (sextets), each associated with a distinct hyperfine field B at the ^{57}Fe nucleus, arising from different configurations of Fe and Pd atoms within the first two coordination shells surrounding the probe nucleus. For the annealed samples, the spectra were fitted with one sextet for pure iron, two sextets for the alloy with $x = 0.0276$, and three sextets for the remaining compositions.

The fitting procedure was based on an additive model, assuming that the contributions of n palladium atoms to both the hyperfine field (B) and the isomer shift (IS) are additive and independent of their specific positions within the first two coordination shells of the Mössbauer probe. Accordingly, the dependence of B and IS on n can be described, respectively, by the following relations

$$B(n) = B_0 + n\ \Delta B_{1,2} \tag{1}$$

and

$$IS(n) = IS_0 + n\ \Delta IS_{1,2}, \tag{2}$$

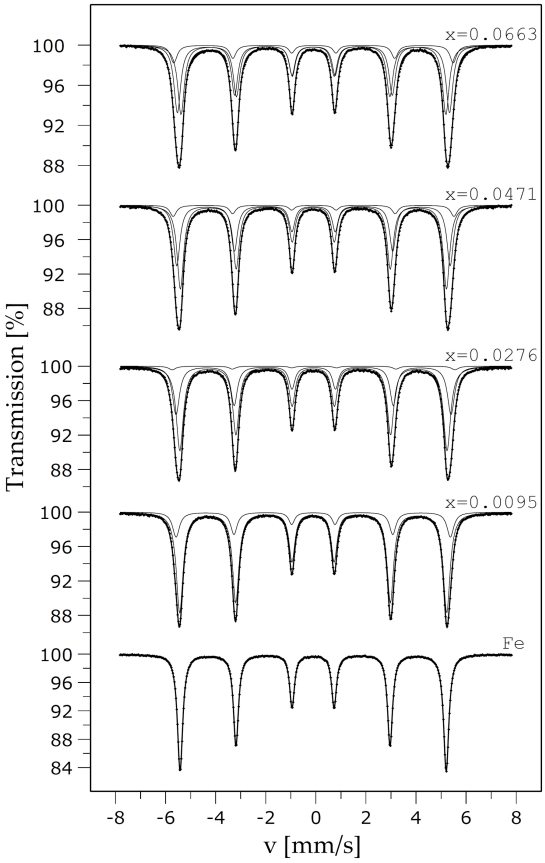

Fig. 1. Room-temperature ^{57}Fe Mössbauer spectra of the $Fe_{1-x}Pd_x$ alloys recorded after annealing at 1270 K followed by slow cooling to room temperature.

where B_0, $\Delta B_{1,2}$, IS_0, and $\Delta IS_{1,2}$ are fitted parameters. Here, $B_0(\Delta B_{1,2})$ and $IS_0(\Delta IS_{1,2})$ stand for the changes in B and IS with zero(one) palladium atom in the first or second coordination shell of the Mössbauer probe. The quadrupole shift for magnetically split spectra (QS) was allowed to vary freely during the fitting and turned out to be nearly zero. The line shapes were assumed to be Lorentzian, with the three widths Γ_{16}, Γ_{25}, and Γ_{34}, together with the two area ratios I_{16}/I_{34} and I_{25}/I_{34}, kept common to all six-line components of a given spectrum. Under these assumptions, satisfactory fits can usually be achieved. In studied alloys, palladium neighbours of the Mössbauer probe have a very small effect on the hyperfine field generated at the probe (see Fig. 1). Consequently, a reliable decomposition of the spectra into individual components cannot be achieved without introducing additional assumptions on the subspectral parameters. A successful analysis of the experimental data was carried out by considering two series of spectra, recorded for samples both in the as-cast state (following arc melting) and after a specific thermal treatment; see [4] for further details. The as-cast samples may be regarded as disordered alloys, for

TABLE I

Hyperfine field and isomer shift parameters obtained for the annealed $Fe_{1-x}Pd_x$ alloys. Standard uncertainties associated with these parameters were determined from the variance of the fitting procedure. Isomer shift values IS_0 are given relative to that of α-Fe at room temperature.

x	B_0 [T]	$\Delta B_{1,2}$ [T]	IS_0 [mm/s]	$\Delta IS_{1,2}$ [mm/s]
0.0095	33.03(10)	0.90(2)	0.001(1)	0.006(2)
0.0276	33.05(10)	0.96(2)	0.008(1)	0.010(1)
0.0471	32.91(10)	0.91(1)	0.008(1)	0.008(1)
0.0663	32.77(10)	0.90(2)	0.008(1)	0.007(1)

which the probability that n atoms of Pd are present among the N atoms in the first coordination shell of a ^{57}Fe probe is given by the binomial distribution

$$p_n = \frac{N!}{(N-n)!\,n!}\; x^n\,(1-x)^{N-n}; \tag{3}$$

for the bcc structure of the studied Fe–Pd alloys, $N = 14$ was adopted. It is worth noting that the fits obtained under these assumptions are quite good. Furthermore, the found values of the best-fit parameters displayed in Table I are in quantitative agreement with corresponding data given in the literature (e.g., in [15, 17, 18]).

From the best-fit hyperfine parameters, the relative intensities c_1 and c_2 were derived for the second and third spectral components. These components reflect configurations with one and two Pd atoms in the two nearest coordination shells of the ^{57}Fe nucleus. Assuming that the Lamb-Mössbauer factor does not depend on the local atomic arrangement, the c_1 and c_2 values represent the intensities of these components. The results are given in Table II.

2.2. The binding energy of two palladium atoms and the enthalpy of solution of palladium in an iron matrix

The parameters c_1 and c_2 obtained from the fits were used to calculate the binding energy E_b of Pd atom pairs in the investigated alloys (Table II). The calculation followed the modified Hrynkiewicz–Królas formula [19] for a $Fe_{1-x}D_x$ system, yielding

$$E_b = -k\,T_d\;\ln\left(\frac{(1+2c_2/c_1)\;c_2/c_1}{(1+2p_2/p_1)\;p_2/p_1}\right). \tag{4}$$

The calculated E_b values are given in Table II.

Subsequently, the binding energy E_b at $x = 0$ was obtained by extrapolation, using the values derived from the experimental data for the Pd-containing samples. The resulting value is $E_b(0) = 0.074(17)$ eV.

TABLE II

The binding energy E_b between a pair of Pd atoms in $Fe_{1-x}Pd_x$ alloys deduced from the ^{57}Fe Mössbauer spectra. Standard uncertainties for c_1 and c_2 result from the variance of the fit of the assumed model to the measured spectra.

x	c_1	c_2
0.0095	0.1991(14)	–
0.0276	0.3550(12)	0.0265(23)
0.0471	0.3891(17)	0.0722(18)
0.0663	0.4366(20)	0.1154(15)
p_1	p_2	E_b [eV]
0.1175	0.0073	–
0.2685	0.0495	0.0652(25)
0.3522	0.1131	0.0440(14)
0.3805	0.1756	0.0475(10)

TABLE III

Enthalpy $H_{\text{Fe-Pd}}$ [eV/atom] of the solution of palladium in iron.

Calorimetric data [14]	Miedema's model [12]	This work
0.177	−0.190	−0.296(68)

This extrapolated quantity was then used to calculate the enthalpy of solution $H_{\text{Fe-Pd}}$ of palladium in iron. The calculation was performed on the basis of the Królas model [9], in which the enthalpy of solution is directly related to the binding energy through the relation

$$H_{\text{Fe-Pd}} = -\frac{1}{2}\,z\,E_b(0), \tag{5}$$

where z is the coordination number of the crystalline lattice ($z = 8$ for α-Fe). Table III summarizes the $H_{\text{Fe-Pd}}$ value obtained in this work, together with the relevant literature data, i.e., calorimetric results for the fcc γ-Fe structure [14] and theoretical estimates derived from Miedema's cellular atomic model [12].

3. Conclusions

The fact that the binding energy between two palladium atoms in the alloys under investigation is positive suggests that, in the ferromagnetic iron host, the interaction between Pd atoms is repulsive at low concentrations (up to about 7 at.% in the present work).

The enthalpy of solution of palladium in iron obtained from the ^{57}Fe Mössbauer spectra (with a value of −0.296(68) eV/atom) shows quite good

quantitative agreement with the value derived from Miedema's model and is at variance with the available calorimetric data for the Fe–Pd system. The result is interesting in that Mössbauer spectroscopy probes the dilute-limit enthalpy of solution of palladium in the ferromagnetic α-Fe (bcc) phase at ≈ 700 K, whereas the calorimetric data refer to iron systems at higher temperatures, where the paramagnetic γ (fcc) phase is stable. This observation may indicate that the experimental $H_{\text{Fe-Pd}}$ value for the Fe–Pd system depends largely on the structural and magnetic state of the matrix, both of which are temperature-dependent.

To the best of our knowledge, the present study reports the first experimental determination of this thermodynamic parameter for the Fe–Pd system in the α (bcc) phase, with atomic configurations frozen at ≈ 700 K, which is below the Curie temperature of iron. This is a significant achievement, as it provides previously unavailable information on the enthalpy of solution and binding energy in the ferromagnetic state of the alloy.

Although no theoretical predictions of $H_{\text{Fe-Pd}}$ for the bcc structure are currently available in the literature, it is our hope that the results presented here will encourage further theoretical investigations. The innovative character of this work is twofold:

(i) it delivers new experimental data that fill a gap in the thermodynamic description of Fe–Pd alloys;

(ii) it demonstrates the potential of Mössbauer spectroscopy as a tool for studying thermodynamic properties even in cases where the spectra are poorly resolved, thus expanding the methodological capabilities of the technique.

References

[1] J. Chojcan, *Hyperfine Interact.* **156/157**, 523 (2004).

[2] E. Jartych, *J. Magn. Magn. Mater.* **265**, 176 (2003).

[3] R. Konieczny, R. Idczak, *Nukleonika* **62**, 9 (2017).

[4] R. Idczak, R. Konieczny, Ż. Konieczna, J. Chojcan, *Acta Phys. Polon. A* **119**, 37 (2011).

[5] R. Konieczny, M. Sobota, R. Idczak, *Acta Phys. Pol. A* **146**, 239 (2024).

[6] R. Konieczny, J. Chojcan, *Acta Phys. Pol. A* **134**, 1053 (2018).

[7] R. Konieczny, R. Idczak, J. Chojcan, *Nukleonika* **60**, 75 (2015).

[8] R. Konieczny, R. Idczak, J. Chojcan, *Acta Phys. Pol. A* **131**, 255 (2017).

[9] K. Królas, *Phys. Lett. A* **85**, 107 (1981).

[10] G. Bonny, R.C. Pasianot, L. Malerba, A. Caro, P. Olsson, M.Yu. Lavrentiev, *J. Nucl. Mater.* **385**, 268 (2009).

[11] R. Boom, F.R. De Boer, A.K. Niessen, A.R. Miedema, *Physica B + C* **115**, 285 (1983).

[12] A.R. Miedema, *Phys. B Condens. Matter* **182**, 1 (1992).

[13] K. Lejaeghere, S. Cottenier, S. Claessens, M. Waroquier, V. Van Speybroeck, *Phys. Rev. B* **83**, 184201 (2011).

[14] R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, K.K. Kelley, *Selected Values of the Thermodynamic Properties of Binary Alloys*, American Society for Metals, Metals Park (OH) 1973.

[15] A. Błachowski, K. Ruebenbauer, J. Żukrowski, *Phys. Scr.* **70**, 368 (2004).

[16] T.E. Cranshaw, *J. Phys. Condens. Matter* **1**, 829 (1989).

[17] I. Vincze, I.A. Campbell, *J. Phys. F* **3**, 647 (1973).

[18] A. Błachowski, U.D. Wdowik, *J. Phys. Chem. Solids* **73**, 317 (2012).

[19] J. Chojcan, *J. Alloys Compd.* **264**, 50 (1998).