Enhanced Compressibility and Pressure-Induced Structural Changes of Nanocrystalline Iron: In Situ Mössbauer Spectroscopy

S. Trapp,[1] C. T. Limbach,[1] U. Gonser,[1] S. J. Campbell,[2] and H. Gleiter[1]

[1]Universität des Saarlandes, FB 15 Werkstoffwissenschaften, D-66041 Saarbrücken, Germany

[2]Department of Physics, University College, The University of New South Wales,
Australian Defence Force Academy, Canberra, ACT 2600 Australia

In situ high pressure (0–1 GPa) Mössbauer spectroscopy has been used to demonstrate for the first time the enhanced compressibility κ of the intercrystalline (IC) regions of nanocrystalline iron compared with that of bulk crystalline α-iron ($\kappa_{IC} \approx 6.6 \kappa_{Fe}$). The component of the Mössbauer spectra due to IC regions exhibits a pressure-induced reversible change of the center shift that is about an order of magnitude larger than that of crystalline bulk α-iron. The effect saturates at pressures above 600 MPa. This change of center shift was removed on pressure annealing the samples, indicating transformation of the interfacial region to a more dense, less compressible structure.

PACS numbers: 76.80.+y, 61.46.+w, 62.50.+p, 81.40.Vw

Nanocrystalline materials consist of two structural components: a crystalline component (CC), which is formed by small single crystals with approximately equiaxed shape, random crystallographic orientations, and dimensions ranging from 5 to 20 nm. The second structural component is the intercrystalline component (IC), which is formed by the boundaries between the crystallites. As described by Gleiter [1], this component is characterized by a reduced atomic density and interatomic spacings deviating from those in the perfect crystal lattice. The IC surrounds the nanometer-sized crystals and forms a network between them.

As a result of the wide range of interatomic spacings and the reduced density in the IC, the interatomic forces are different compared with a crystalline material of the same chemical composition. If an external pressure is applied to a nanocrystalline material, the interatomic spacings in the IC are expected to be reduced by a greater amount than those in the CC due to the lower density of the IC. Hence, by studying the compressibility of the IC relative to the CC we may be able to obtain new insight to the structure and the behavior of the IC in nanocrystalline materials. The aim of this Letter is to report the first investigation of the compressibility of the IC of nanocrystalline iron by means of Mössbauer spectroscopy with and without externally applied pressures.

Mössbauer spectroscopy was chosen because it reveals structural changes on an atomic scale with high resolution, and permits in situ pressure measurements. Moreover, it conveniently distinguishes between the spectral components of the IC regions and the crystalline cores ([2], see also [3] for a review).

The nanocrystalline iron pellets were prepared by the high pressure compaction (1 GPa) of iron nanocrystals produced by inert gas condensation (see Ref. [4]). After compaction the iron pellets were transferred directly from the vacuum chamber into heptane in order to minimize oxidation.

The average grain size of the nanocrystalline iron was determined by applying the Scherrer formula to the experimentally observed line broadening of the x-ray reflections (see Ref. [5]). The grain size was found to be about 7 nm for all samples studied in the as-prepared state. A slight increase in the grain size to about 9 nm was observed following the pressure annealing experiments outlined below. In addition, the average grain size of the annealed sample (170 °C, for 24 h with external pressure) was determined by dark field transmission electron microscopy and was found to be 11 nm. The impurity contents of the samples were checked by energy dispersive x-ray analysis. Tungsten, with a concentration level of less than 1 at.% (i.e., near the detection limit of the technique), was the only impurity element observed.

The Mössbauer spectra of the iron pellets under various pressures were measured using a high pressure cell with γ-ray transparent boron-carbide pistons [6]. The pellet was mounted between two pistons, the first supported by the bottom of the pressure cell, with the second piston applying the force by means of three cup springs under compression from a fine thread clamp screwed into the housing. The cup springs were loaded using a tension test machine and the clamp screwed onto them by hand. The compressed springs could then apply a constant pressure to the pellet through the pistons. The pressure was controlled after each experiment by applying the original force to the springs in order to open the clamp by hand. The error was estimated to be less than 2 MPa. Because of the very large number of grain boundaries in a pellet, all with a different orientation relative to the main force direction, the applied pressure can be considered hydrostaticlike. The Mössbauer spectrum of the pistons alone was measured with and without pressure, and no change in its three doublets was found. These resulting parameters were adopted for all other experiments. The pressure cell was installed in a Mössbauer-transmission spectrometer. The γ rays from the ^{57}CoRh source were detected by an

    0031-9007/95/75(20)/3760(4)$06.00

argon-methane proportional counter and the spectrometer calibrated using a standard α-iron foil. The isomer shift values are quoted relative to the center of the α-iron spectrum. The experiments were carried out in two series. In the first set of measurements, labeled series 1, the pressure dependence of the Mössbauer spectrum of a nanocrystalline iron pellet was determined at ambient temperature. In the second set of experiments, series 2, the structural relaxation behavior of the nanocrystalline iron was studied by annealing the samples under pressure, with the spectra subsequently being measured at room temperature (296 K).

Series 1.—The Mössbauer spectra were monitored while the nanocrystalline iron was subjected to various applied pressures of up to 1000 MPa. Two main subspectra were observed at all pressures with one being due to the CC and the other to the IC. In addition, five other (weak) impurity subspectra were noticed—two of them are identified with small amounts of the Fe_3O_4 spectrum with the other three being doublets originating from residual iron contaminations of the boron-carbide pistons. The spectra were fitted using standard least squares methods, and, in the case of the broadened magnetic hyperfine subspectra, they were fitted using a distribution of magnetic hyperfine fields [7,8]. The hyperfine parameters of the CC and these five weak impurity subspectra (see Table I) did *not* change when the pressure was applied. On the other hand, the subspectrum of the IC was found to change with pressure (see Table II) with the center shift δ_{CS} of the IC changing significantly with pressure (Fig. 1).

At ambient pressure the center shift δ_{CS} of the IC is positive compared with bulk α-iron, indicating a reduced atomic density in the boundaries. Above about 100 MPa (Fig. 1) δ_{CS} becomes negative. The pressure-induced variation of δ_{CS} of the IC was found to be completely reversible. In fact, experiment 3 (Fig. 1) reveals that δ_{CS} returns to positive values when the sample is nearly unloaded. The center shift δ_{CS} shows a saturation behavior above a pressure of about 600 MPa. In contrast to the changes observed for δ_{CS}, no significant pressure dependence of the mean magnetic hyperfine field (B_{hf}), the quadrupole splitting (QS), or the volume fraction of the IC was observed (Table II).

TABLE I. The hyperfine parameters of the CC subspectrum and the impurity subspectra of nanocrystalline iron subject to pressure at ambient temperature. (B_{hf} is magnetic hyperfine field, δ_{CS} center shift, QS quadrupole splitting, and Γ linewidth.)

Component	B_{hf} (T)	δ_{CS} (mm/s)	QS (mm/s)	Γ (mm/s)
Crystalline component	32.9	0.01	0.00	0.35
Fe_3O_4	45.0	0.66	-0.03	0.35
	48.2	0.27	0.02	0.35
$B_4C(Fe)$-type	$\cdots$	0.30	0.43	0.35
$B_4C(Fe)$-type	$\cdots$	0.21	1.91	0.35
$B_4C(Fe)$-type	$\cdots$	0.41	2.89	0.35

Series 2.—The annealing experiments of series 2 were designed to study relaxational effects of the nanocrystalline iron pellets with particular interest centered on the behavior of the IC. All Mössbauer spectra of this series were fitted to nine subspectra (cf. Fig. 2) using the programs of Brand [9] and Hába [10]. Six of the subspectra can be readily related to crystalline components as for the series 1 spectra—CC, two components of the iron oxide and the iron impurities in the B_4C pistons. For the IC subspectrum, line broadening up to $\Gamma \approx 1.22$ mm/s was obtained. Two other subspectra, each a six line magnetically split subspectrum of $B_{hf} \geq 35$ T and total contribution to the entire spectrum of <5%, are probably due to impurity iron oxides and are not considered further, as they stay stable over all experiments.

The experiments were carried out as follows: above the saturation pressure of 600 MPa (observed in series 1) the pressure cell was removed from the spectrometer and annealed at 170 °C for 24 h at a pressure of 860 MPa. After this heat treatment δ_{CS} of the IC was again measured under pressure and was found to be unchanged. When unloading the cell, δ_{CS} remained at the same (negative) value (cf. Fig. 3). This observation indicates an enhancement of the atomic density in the boundaries during annealing compared with that of the IC regions in the original as-prepared nanocrystalline state. The hyperfine parameters of all other subspectra were found to remain constant dur-

TABLE II. The hyperfine parameters of the IC subspectrum of nanocrystalline iron subject to the pressures listed (δ_{CS} is found to change significantly with pressure; cf. Fig. 1).

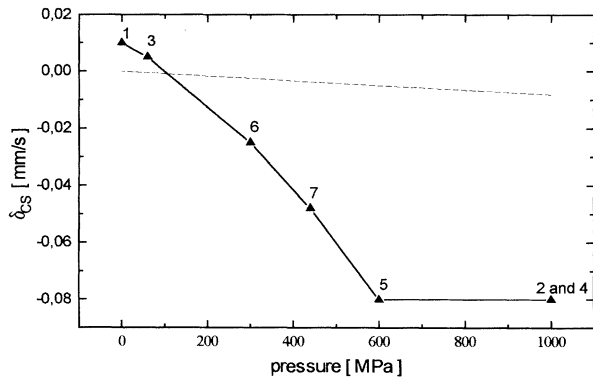| Experiment	Pressure (MPa)	B_{hf} (T)	δ_{CS} (mm/s)	QS (mm/s)	Γ (mm/s)	Fraction (%)
1	0	33.8	0.010	-0.02	0.30	52
2	1000	32.9	-0.080	-0.04	0.25	51
3	60	33.9	0.005	-0.01	0.25	45
4	1000	33.2	-0.080	-0.04	0.25	50
5	600	33.2	-0.080	-0.03	0.25	49
6	300	33.2	-0.025	-0.03	0.25	44
7	440	33.9	-0.048	-0.02	0.25	47

FIG. 1.   The center shift δ_{CS} of the intercrystalline component of nanocrystalline iron as a function of pressure. The numbers above the points (filled triangles) indicate the sequence of the measurements (cf. Table II). The resolution is 0.01 mm/s. The change of δ_{CS} for bulk α-iron as determined by Pound, Benedek, and Drever [13] is also plotted (dots).

ing this series of experiments. As mentioned already, all spectra were recorded at ambient temperature (296 K).

Based on the values of δ_{CS} of series 1 experiments, the compressibility of the IC may be estimated as follows. As described by Barb [11], the pressure dependence of δ_{CS} is given by

$$\left(\frac{\partial \delta_{CS}}{\partial p}\right)_T = \left(\frac{\partial \delta_{IS}}{\partial p}\right)_T + \left(\frac{\partial \delta_{SOD}}{\partial p}\right)_T, \qquad (1)$$

where δ_{IS} is the isomer shift and δ_{SOD} is the second order Doppler shift.
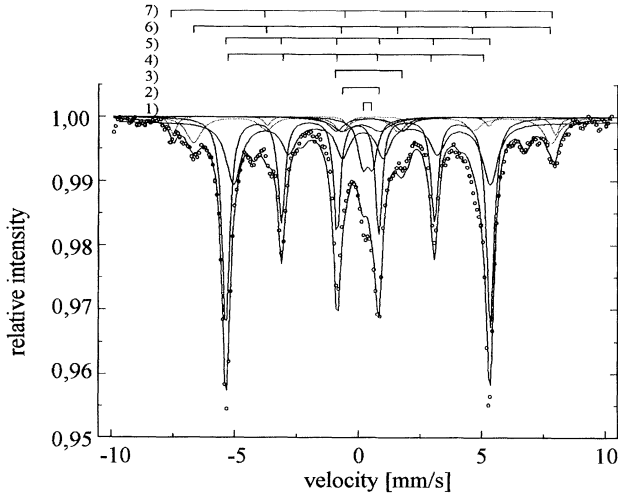

FIG. 2.   A Mössbauer spectrum (80 MPa, 296 K) from the series of pressure annealing experiments (series 2) on nanocrystalline iron. Circles: measured points; (1), (2), (3): Doublets from iron impurities in the B_4C pistons; (4): subspectrum of the intercrystalline component; (5): subspectrum of the crystalline component; (6) and (7): subspectral components of Fe_3O_4 [17].

A correlation to the thermal compressibility can be obtained by

$$\left(\frac{\partial \delta_{CS}}{\partial p}\right)_T = -\kappa\left[\left(\frac{\partial \delta_{IS}}{\partial \ln V_a}\right)_T + \left(\frac{\partial \delta_{SOD}}{\partial \ln V_a}\right)_T\right], \qquad (2)$$

where V_a is the atomic volume and the isothermal compressibility κ being given by

$$\kappa = -\frac{1}{V_a}\left(\frac{\partial V_a}{\partial p}\right)_T. \qquad (3)$$

The two terms within the brackets of Eq. (2) are the volume coefficients of the isomer shift and the second order Doppler shift, respectively (Vc_{IS} and Vc_{SOD}) (see Ref. [12]). The upper bounds for Vc_{IS} and Vc_{SOD} may be estimated as follows. For bulk α-iron, Vc_{IS} is 1.37 mm/s (see Ref. [13]), and for ε-iron, which is 8% more dense than α-iron, Vc_{IS} is 0.8 mm/s as determined by Williamson, Bukshpan, and Ingalls [14]. Extrapolating this density variation of Vc_{IS} to a density of about 70% of that of α-iron, leads to a value of $Vc_{IS} \approx 3.5$ mm/s. A density of 70% of that of α-iron is the lowest density limit in grain boundary cores estimated by Fecht [15] on the basis of theoretical models. Hence, 3.5 mm/s represents an upper limit for Vc_{IS} in the intercrystalline boundary regions of nanocrystalline iron. Vc_{SOD} for the IC may be estimated by the approach outlined by Williamson, Bukshpan, and Ingalls in [14]. Assuming a maximum value for the Grüneisen constant for grain boundary cores of 8 (see Ref. [15]), Vc_{SOD} is found to be about 0.8 mm/s for the IC.

Based on these values and using $\delta_{CS} = -0.09$ mm/s for $\Delta p = 600$ MPa (the difference of δ_{CS} between the unloaded state and the saturation load at 600 MPa in series 1; Table II) the minimum value for the isothermal compressibility κ_{IC} if the IC is

$$\kappa_{IC} = 4.0 \times 10^{-11} \text{ Pa}^{-1}.$$

Comparing this result with the bulk compressibility of α-iron (κ_{Fe}) leads to

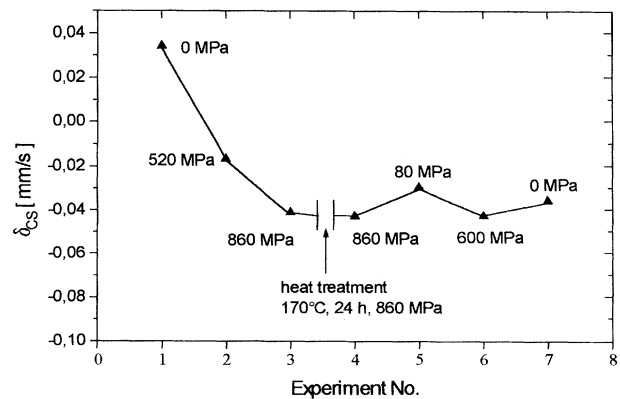$$\kappa_{IC} \approx 6.6\kappa_{Fe}.$$

FIG. 3.   The pressure dependence of δ_{CS} of the intercrystalline component before and after a heat treatment at 170 °C for 24 h.

Indeed if less conservative assumptions are made about Vc_{IS}, Vc_{SOD}, and δ_{CS}, larger values for the compressibility of the interfacial component are obtained. This result demonstrates the remarkable enhancement in the compressibility of the grain boundary regions in nanocrystalline iron. For comparison, the compressibility of iron increases by a factor of about 1.6 upon melting [16].

These results indicate that the boundary regions of nanocrystalline iron are characterized by a reduced atomic density. This interfacial region of reduced density can be compressed readily until the repulsive forces act between the atoms in the boundaries to limit further compression. On annealing, the atomic structure of the interfacial regions changes to a less compressible and probably more dense structure as evidenced by the enduring negative values for δ_{CS} (Fig. 3). This structural transformation on pressure annealing occurs with little or no grain growth (evidence for only a slight increase in the grain size from ≈ 7 to ≈ 11 nm was noticed; nor indeed was any change observed in the fraction of area of the IC of the Mössbauer spectra). Such behavior is not found for bulk crystalline or glassy iron, indicating that the effective elastic constants of intercrystalline regions differ from those of crystalline or glassy iron.

[1] H. Gleiter, in *Mechanical Properties and Deformation Behaviour of Materials Having Ultra-Fine Microstructures,* edited by H. Nastasi *et al.* (Kluwer Academic Publishers, Dordrecht, 1993), p. 3.

[2] U. Herr, J. Jing, R. Birringer, U. Gonser, and H. Gleiter, Appl. Phys. Lett. **50**, 472 (1987).

[3] S.J. Campbell and H. Gleiter, in *Mössbauer Spectroscopy Applied to Magnetism and Materials Science,* edited by G.J. Long and F. Grandjean (Plenum Press, New York, 1994), Vol. 1, p. 241.

[4] H. Gleiter, in *Progress Material Science,* edited by J.W. Christian, P. Haasen, and T.B. Massalski (Pergamon Press, New York, 1989), Vol. 33, p. 228.

[5] L. Azaroff, *Elements of X-ray Crystallography* (McGraw-Hill, New York, 1968), p. 557.

[6] J.S. Schilling, U.F. Klein, and W.B. Holzapfel, Rev. Sci. Instrum. **45**, 11 (1974).

[7] J. Hesse and A. Rübartsch, J. Phys. E **7**, 526 (1974).

[8] G. Le Caer and J.M. Dubois, J. Phys. E **12**, 1083 (1979).

[9] R.A. Brand, Normos Programs, IFF der KFA Jülich, Federal Republic of Germany, 1989.

[10] Z. Hába, INTF Programs, Joint Laboratory of Mössbauer Spectroscopy, Faculty of Mathematics and Physics, Prague 8, Czech Republic, 1993.

[11] D. Barb, in *Grundlagen und Anwendungen der Mössbauerspektroskopie,* edited by W. Meisel (Academie-Verlag, Berlin, 1980), p. 150.

[12] D.L. Williamson, in *Mössbauer Isomer Shifts,* edited by G.K. Shenoy and F.E. Wagner (North-Holland Publishing Company, Amsterdam, 1978), p. 317.

[13] R.V. Pound, G.B. Benedek, and R. Drever, Phys. Rev. Lett. **7**, 405 (1961).

[14] D.L. Williamson, S. Bukshpan, and R. Ingalls, Phys. Rev. B **6**, 4194 (1972).

[15] H.J. Fecht, Acta Metall. Mater. **38**, 1927 (1990).

[16] R.L. Parker and J.R. Manning, J. Cryst. Growth **79**, 341 (1986).

[17] N.N. Greenwood and T.C. Gibb, *Mössbauer Spectroscopy* (Chapman and Hall Ltd., London, 1971), p. 251.