University of Groningen

Iron nanoparticles grown in a carbon arc discharge

Zhang, G.L.; du Marchie van Voorthuysen, E.H.; Szymanski, K.; Boom, G; Verwerft, M.G M; Jonkman, H.T.; Niesen, L

Published in:

Nuovo Cimento Della Societa Italiana di Fisica. D: Condensed Matter Atomic Molecular and Chemical Physics
Fluids Plasmas Biophysics

DOI:

[10.1007/BF02458905](https://doi.org/10.1007/BF02458905)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version

Publisher's PDF, also known as Version of record

Publication date:

1996

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Zhang, G. L., du Marchie van Voorthuysen, E. H., Szymanski, K., Boom, G., Verwerft, M. G. M., Jonkman, H. T., & Niesen, L. (1996). Iron nanoparticles grown in a carbon arc discharge. *Nuovo Cimento Della Societa Italiana di Fisica. D: Condensed Matter Atomic Molecular and Chemical Physics Fluids Plasmas Biophysics*, 18(2-3), 281 - 285. <https://doi.org/10.1007/BF02458905>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Iron nanoparticles grown in a carbon arc discharge (*)

G. L. ZHANG, E. H. DU MARCHIE VAN VOORTHUYSEN, K. SZYMANSKI, G. BOOM
M. G. M. VERWERFT, H. T. JONKMAN and L. NIESEN

*Materials Science Centre, Rijksuniversiteit Groningen
Nijenborgh 4, 9747 AG Groningen, The Netherlands*

(ricevuto il 27 Settembre 1995)

Summary. — Iron particles, encapsulated by graphite layers, were produced by means of the Kratschmer arc discharge method in an iron pentacarbonyl atmosphere. The Mössbauer effect is dominated by the vibration of the particles as a whole. Superparamagnetism is dominant for iron oxide particles. No endohedral iron fullerenes were observed, contrary to a previous report.

PACS 75.60.Jp - Fine particle systems.

PACS 76.80 - Mössbauer effect; other γ -ray spectroscopy.

PACS 43.40 - Structural acoustics and vibration.

PACS 01.30.Cc - Conference proceedings.

Particles of metallic iron and iron compounds, partially wrapped in layers of graphite, were produced by a carbon arc (20 V, 100 A) in a helium atmosphere of 50 mbar. Kratschmer *et al.* [1] used this method for the first time to produce fullerenes. The vessel was connected to a container with $\text{Fe}(\text{CO})_5$ liquid. By varying the temperature the partial pressure of the $\text{Fe}(\text{CO})_5$ vapour was varied from 100 to 400 mbar for different production runs. The production vessel was kept at 80 °C with hot water in order to prevent condensation of $\text{Fe}(\text{CO})_5$ against the wall. The soot that became deposited on the wall was collected and used for a large number of measurements. The iron concentration in the soot, measured by means of an atomic spectrometric method, varied from 2 to 12 weight % for the different production runs.

The fullerene content was extracted from the soot using toluene. Mass spectroscopy was performed resulting in a normal yield of C_{60} and C_{70} , but no $\text{Fe}@\text{C}_{60}$ or $\text{Fe}@\text{C}_{70}$ molecules were observed, the probability that a C_{60} molecule is bound to a Fe atom was less than 0.01%. We conclude that the recipe of Pradeep *et al.* [2] is inadequate to produce endohedral iron.

(*) Paper presented at ICAME-95, Rimini, 10-16 September 1995.

Fig. 1. - Mössbauer spectra of nanoparticles. *a*) Sample B non-oxidised ($T = 5.3$ K), *b*) sample AO oxidised ($T = 4.7$ K), *c*) sample AO oxidised ($T = 9.5$ K) showing superparamagnetic relaxation.

In this paper we report measurements on three different samples of iron-containing particles in soot. Sample A, containing 7.1 weight % iron, was produced at a $\text{Fe}(\text{CO})_5$ pressure of 370 mbar, sample AO is the same material after oxidation, and sample B (3.1 weight % Fe) was produced at 220 mbar.

The particles were observed by means of electron microscopy. The sizes varied from 10 to 180 nm, the larger particles probably are conglomerates of smaller particles. With HREM the carbon encapsulation and the identity of a few particles could be determined. We recognised cementite and austenite.

Mössbauer measurements were performed in transmission geometry as a function of temperature of the soot using a flow cryostat and a 5 mCi $^{57}\text{CoRh}$ source. The soot was pressed into perspex holders with a pressure of ≈ 3 bar. Figure 1 shows three Mössbauer spectra. The main components in the spectra at liquid-helium temperature of the non-oxidised samples A and B are martensite (BCT iron) and cementite (Fe_3C).

Fig. 2. - Hyperfine field as a function of temperature of the non-oxidised sample B. Least-squares fits to linear functions. ● Martensite; ▲ cementite; ○ Fe₂O₃.

About 15% is ferrimagnetic γ -Fe₂O₃, About 10% is non-magnetically split: austenite (f.c.c. iron with a small percentage of carbon) and superparamagnetic martensite, cementite and γ -Fe₂O₃. The main components of the spectrum at liquid-helium temperature of sample AO are iron oxides with hyperfine fields ranging from 40 to 50 T.

The Mössbauer spectra are dominated by ferromagnetic sextets. The absorption lines from the non-oxidised samples are sharp, fig. 1a), but the sextet from the oxidised sample AO has very broad lines and can be fitted only by assuming a distribution of hyperfine fields, fig. 1b). With increasing temperature the intensities of the non-magnetically split components increase to the detriment of the sextets because of superparamagnetic relaxation. At 11.2 K the intensities are equal; at this temperature the assembly of nanoparticles is at the borderline between the stable regime and the superparamagnetic regime for the Mössbauer effect. Using eq. (2) of ref.[3] and assuming a magnetic anisotropy constant $K = 10^5$ J/m³ we calculate an average particle diameter of 1.9 nm.

The superparamagnetic relaxation is much smaller for the non-oxidised samples A and B; even at room temperature the sextets are dominating the spectra. In fig. 2 the measured hyperfine field is plotted as a function of temperature. The decrease of B_{HF} at increasing temperature has two causes: the decrease of spontaneous magnetisation

according to Bloch's $T^{3/2}$ law and the onset of superparamagnetism, causing a broadening of the distribution of the momentaneous magnetisation directions around the easy directions within the particles at increasing temperature. The B_{HF} reduction brought about by this effect is proportional to the anisotropy ΔE [4,5]. We fitted the experimental hyperfine fields to a linear function of temperature. The third column in table I gives the relative slopes. The fourth column gives the relative reduction in spontaneous magnetisation, and from the difference we calculated the magnetic anisotropy barrier ΔE and from that the average particle size, assuming again $K = 10^5 \text{ J/m}^3$.

TABLE I. - Calculation of average particle sizes from the measured hyperfine field as a function of temperature for sample B.

	B_0 (T)	$\frac{dB_{\text{HF}}}{dT} / B_0$ (K^{-1})	Spontaneous magnetisation reduction (K^{-1})	ΔE (J)	Diameter (nm)
martensite	34.53(4)	$-1.04 \cdot 10^{-4}$	$-0.61 \cdot 10^{-4} (b)$	$16.1(5) \cdot 10^{-20}$	14.5
cementite ^(a)	25.7(2)	-2.31	-2.3 ^(c)	> 17	> 15
$\gamma\text{-Fe}_2\text{O}_3$	51.9(2)	-4.32	-1.5 ^(d)	1.9(1)	7.8

(a) Only analysed for $T < 110 \text{ K}$; (b) ref. [6]; (c) ref. [7] using $T_c = 483 \text{ K}$; (d) using Mössbauer data from Fe_3O_4 [8].

The Debye temperatures of iron and most of its compounds are in the region of 470 K. So the overall Mössbauer effect will decrease only about 12% when the temperature increases from 4 K to room temperature.

However, we always observed a much larger decrease, fig. 3 gives the total absorption of sample B, normalised with the recoilless fraction according to the Debye model with $Q = 470 \text{ K}$. Bulk material would give a constant absorption in fig. 3, but here we see the effect of particle vibrations. We apply a model in which the assembly consists of two fractions with different spring constants, the curve in fig. 3 is given by the function $A(T) = 25 \exp [-0.038 T] + 80 \exp [-0.00133 T]$. It is mainly the cementite fraction that causes the fast decrease at low temperatures. Using the formulae from ref.[9] we calculate a spring constant $q = 2.0 \text{ J/m}^2$ for the soft fraction and $q = 55 \text{ J/m}^2$ for the hard fraction, which is dominant at high temperature. From the minimum size of the cementite, 15 nm,

Fig. 3. - Total absorption of sample B divided by the recoilless fraction for $Q = 470 \text{ K}$.

and assuming a density of 5000 k/m^3 , we calculate an average vibration frequency smaller than 2 GHz for the cementite particles in sample B.

The very fast decrease of the Mössbauer effect that we observed for a substantial fraction of the nanoparticles, which is caused by particle vibration amplitudes in the order of ångströms, may be the consequence of the encapsulation of the particles. The particles are formed at very high temperature, where the cementite (melting point 1840°C) may be a liquid drop inside the solid graphite encapsulation (melting point 3550°C). During the solidification and cooling down the contraction of the particle is larger than for the encapsulation, so empty space is created inside the graphite in which the particle can easily vibrate with large amplitudes, see also [10].

REFERENCES

- [1] KRATSCHMER W., LAMB L. D., FOSTIROPOULOS K. and HUFFMAN D. R., *Nature*, **347** (1990) 354.
- [2] PRADEEP T., KULKARNI G. U., KANNAN K. R., GURU ROW T. N. and RAO C. N. R., *J. Am. Chem. Soc.*, **114** (1992) 2272.
- [3] KNELLER E. F. and LUBORSKY F. E., *J. Appl. Phys.*, **34** (1963) 656.
- [4] MØRUP S. and TOPSØE H., *Appl. Phys.*, **11** (1976) 63.
- [5] BØDKER F., MØRUP S. and LINDEROTH S., *Phys. Rev. Lett.*, **72** (1994) 282.
- [6] ALDRED A. T. and FROEHLE P. H., *Int. J. Magn.*, **2** (1972) 195.
- [7] SHIGEMATSU T., NAKANISHI N. and KACHI S., *J. Phys. Soc. Jpn.*, **35** (1973) 1250; **37** (1974) 940.
- [8] HÄGGSTRÖM L., ANNERSTEN H., ERICSSON T., WÄPPLING R., KARNER W. and BJARMAN S., *Hyperfine Interact.*, **5** (1978) 201.
- [9] BØDKER F., MØRUP S., OXBORROW C. A., LINDEROTH S., MADSEN M. B. and NIEMANTSVERDRIET J. W., *J. Phys.: Condens. Matter*, **4** (1992) 6555.
- [10] SAITO Y., YOSHIKAWA T., OKUDA M., OHKOHCHI M., ANDO Y., KASUYA A. and NISHINA Y., *Chem. Phys. Lett.*, **209** (1993) 72.