

# Magnetic iron-containing nanoparticles on the surface of multiwalled carbon nanotubes

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**Abstract** Based on the temperature dependence of the hyperfine parameters of the  $^{57}\text{Fe}$  nuclei, the qualitative and quantitative phase composition of nanocrystalline iron oxides on the surface and on the tails of the “classic” multiwalled carbon nanotubes (CNT) was investigated. From the observed temperature dependence it was shown that the contribution of the nonmagnetic iron-containing phase is caused by small size nanoparticles on the CNTs surface.

**Keywords** Multiwalled carbon nanotubes · Mössbauer spectroscopy · Iron oxides

## 1 Introduction

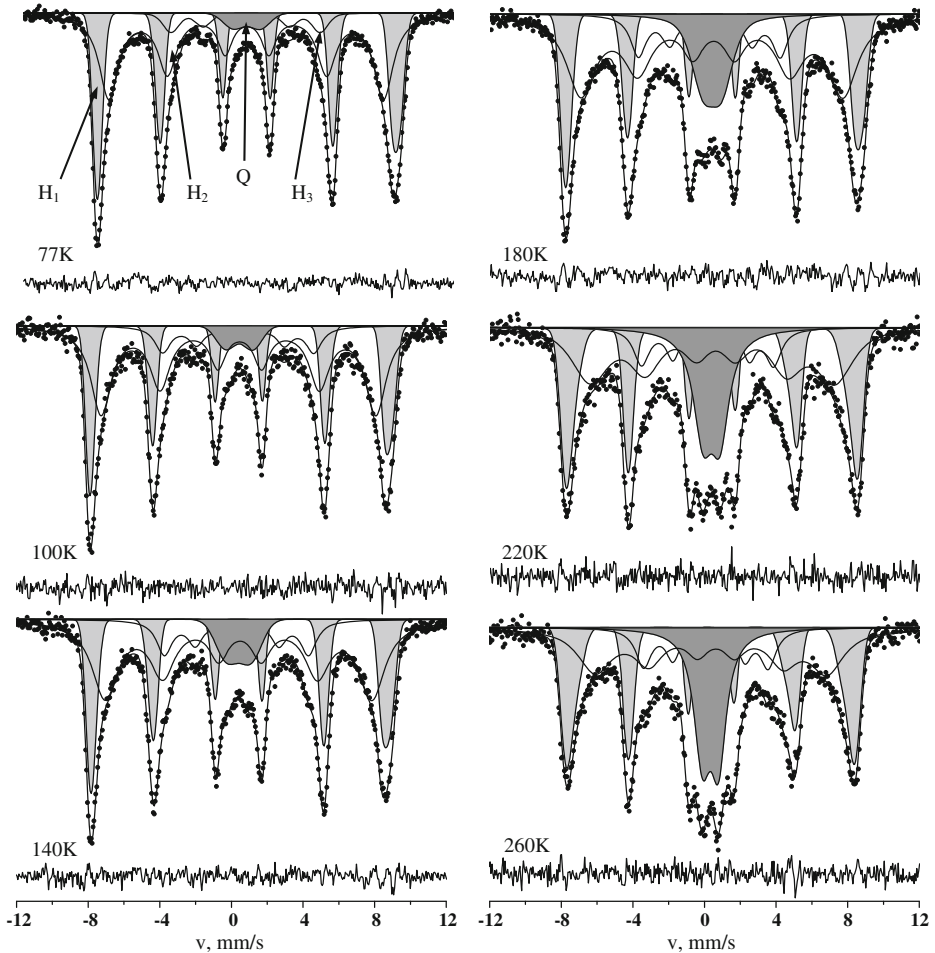
The application of micro- and nanometer magnetic materials based on complex metal oxides is currently one of the most important areas of modern physics and chemistry of materials and electronics. In addition, a special interest in the study of oxide particles of such size on the surface of an inert carrying base is aroused due to the possibility of the application of such objects in catalytic processes [1]. One of such systems is maghemite, which is oxide  $\gamma\text{-Fe}_2\text{O}_3$  with spinel structure.

## 2 Experimental

The synthesis of iron-containing CNTs was performed on an injection unit following the procedure described in [2]. A mixture of acetylacetonate Fe(II) in benzene and ethanol solution was used as a precursor and nitrogen gas was used as purge gas. The synthesis temperature was 900–950 K.

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**Fig. 1**  $^{57}\text{Fe}$  Mössbauer spectra of carbon nanotubes at different temperatures

### 3 Results and discussion

$^{57}\text{Fe}$  Mössbauer spectra of the obtained samples of CNTs, measured over a wide temperature range (Fig. 1), represent a complex magnetic structure consisting of several magnetic subsystems. According to electron microscopy, the particle size varies in the range 5–40 nm, so the analysis of an experimental Mössbauer spectra of these particles which is often carried out by introducing a distribution function of hyperfine magnetic fields or by computing with a model of a superposition of discrete subspectra, does not allow a satisfactory fit. In the analysis of such distributions, it is possible to establish maximum and average hyperfine magnetic fields on the  $^{57}\text{Fe}$  nuclei. However, in the case of multiphase nanosystems there can be a loss of quantitative and qualitative information about the composition of the samples when introducing a distribution function  $P(H)$ , especially when there are significantly different values of isomer shifts ( $\delta$ ), quadrupole shifts ( $\epsilon$ ) of Zeeman sextets involved.

Therefore, the Mössbauer spectra were analysed in the framework of the superposition of three magnetic subspectra ( $H_1$ ,  $H_2$ ,  $H_3$ ) and a quadruple doublet (Q). The magnetic subspectrum corresponding to hyperfine field  $H_1$  was fitted as a quasidistribution of hyperfine magnetic fields  $P(H)$  with their parameters corresponding to iron oxide  $\gamma\text{-Fe}_2\text{O}_3$ . During the fitting procedure of this component relations were imposed on the ratio of the partial sextets in this component, in accordance with the population of the cationic positions in the structure of  $\gamma\text{-Fe}_2\text{O}_3$  being equal to 2:1 [3], as well as on the difference in isomer shift ( $\Delta\delta$ ), which was set to 0.13 mm/s for this compound [3]. The analysis of the dependence of the average hyperfine field ( $\langle H \rangle$ ) on temperature, as well as the average linewidth ( $\langle \Gamma \rangle$ ) for this component is consistent with the data of electron microscopy and indirectly confirms the assumption of a fairly wide size distribution of iron oxide nanoparticles  $\gamma\text{-Fe}_2\text{O}_3$ . From the analysis of the temperature dependence of the isomer shift the temperature coefficient of the isomer shift  $d\delta/dT = -(6.4 \pm 0.5) \cdot 10^{-4} \text{ mm} \cdot \text{s}^{-1} \cdot \text{K}^{-1}$  was determined for the  $^{57}\text{Fe}$  nuclei in this subspectra.

The second magnetic component  $H_2$  of the spectrum, with a large area, represents a strongly broadened Zeeman sextet with the hyperfine parameters ( $\delta$ ,  $\varepsilon$ ) which correspond to  $\text{Fe}^{3+}$  cations being in an oxygen environment [3]. An accurate identification of this phase in this case is difficult, however, considering the very significant decrease in the amount of this component with increasing temperature. Since the carbon nanotubes on the surface of iron particles are on the average smaller in comparison with iron-containing nanocrystallites at the CNTs tails, we can assume that the features of the formation of nanoparticles of iron oxides in various parts of the tubes are different in terms of synthesis conditions.

Finally, the third magnetic component  $H_3$  hyperfine parameters correspond to the  $\text{Fe}_3\text{C}$  compound [4], but the temperature change of the hyperfine magnetic field of this component as well as in the case of  $H_1$  and  $H_2$  is quite different from “classic” Brillouin-type systems. Such behavior of the hyperfine magnetic field for all magnetic subspectra indirectly confirms the nanocrystalline nature of all of the particles of iron-containing phases.

In addition, it should be noted that the spectrum has no relaxation component represented by a magnetic sextet, which is characterized in the simplest case of superferromagnetism by a flip time ( $\tau$ ) of the magnetic moment and has an activation character ( $\tau = \tau_0 \exp(|K_e|V/kT)$ ) [5]. Although the appearance in the spectra of nanoparticles of such a relaxation component is expected, however, in the case of our broad distribution of particle sizes, the amount of such a component may be negligible in comparison with the magnetic and paramagnetic components.

## 4 Conclusion

Thus, on the basis of studies we have shown that nanocrystalline particles of  $\gamma\text{-Fe}_2\text{O}_3$  with a wide size in distribution are formed on the surface of CNTs. It is established that these particles are mainly localized at the tails of the nanotubes. Also the presence of polycrystalline phase  $\text{Fe}_3\text{C}$  was shown, which subspectrum contribution is practically independent from temperature changes. It was shown that the main phase transfer from magnetic ordered phase into a non-magnetic components is reflected in the decrease of the  $H_2$  component contribution in the overall spectrum.

Using this dependence it can be concluded that small (20 nm) ( $H_2$  component) iron oxide particles, comparable to  $\gamma\text{-Fe}_2\text{O}_3$ , are located on the CNTs surface.

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## References

1. Serp, P., Corrias, M., Kalck, P.: *Appl. Catal. A Gen.* **253**, 337 (2003)
2. Savilov, S.V., Zosimov, G.A., Lunin, V.V.: RF Patent No. 2310601 (2007)
3. da Costa, G.M., De Grave, E., Vandenberghe, R.E.: *Hyperfine. Interact.* **117**, 207 (1998)
4. Bauer-Grosse, E., Le Caer, G., Fournes, L.: *Hyperfine. Interact.* **27**, 297 (1986)
5. Predoi,  $\hat{A}$ ., Kuncser, V., Filoti, G.: *Rom. Rep. Phys.* **56**, 373 (2004)