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Low-temperature stable nanometer-size fcc-Fe particles with no magnetic ordering

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Nanometer-size iron particles (~8 nm diameter) with the face-centered-cubic (fcc) structure were made using a technique based on the transversely excited atmospheric CO_2-laser-induced breakdown of $Fe(CO)_5$. This fcc γ-Fe phase is extremely stable based on observations over three years. Mössbauer spectra over a small velocity range with and without a magnetic field applied show that these nanometer fcc-Fe particles are paramagnets down to a temperature of 1.8 K. This result supports theoretical predictions that the ground state of fcc iron depends strongly on the volume.

Currently nanometer-scale systems are of great interest since they may possess properties that differ substantially from those of bulk material. This paper is concerned with the magnetic properties of nanometer-size iron particles with the face-centered-cubic structure, a phase not normally stable at and below room temperature. Evidence, based on Mössbauer spectroscopy, will be presented that these fcc γ particles, made by a laser technique, remain paramagnetic even below the temperature of liquid helium (4.2 K).

Bulk pure iron takes two different crystal structures at atmospheric pressure, viz., body-centered cubic (bcc), both at temperatures below 1183 K and at temperatures above 1663 K up to the melting point of 1807 K, and face-centered cubic (fcc) at temperatures between 1183 and 1663 K (the γ phase). Below the Curie point, $T_f = 1096$ K, bcc Fe is a ferromagnet (the α phase); above T_f bcc Fe is a paramagnet (the β phase).[1] The phase above 1663 K is called the δ phase. In addition to these phases, a hexagonal-close-packed (hcp) structure (the ε phase), a paramagnet at room temperature, is reported to exist at high pressures.[2]

The focus here is on the fcc γ phase of metallic iron. Even for bulk iron, the origin of the α to γ (or γ to α) phase change is uncertain. Theories proposed consider either vibrational (nonmagnetic) or magnetic contributions to the free energy. More recently, by starting with the Hubbard single-band model and including entropy changes, a phase diagram has been calculated for bulk iron that is similar to that observed experimentally.[3]

Several attempts have been made to establish the magnetic properties of the fcc phase of iron at temperatures lower than those at which it is stable when in the bulk state. Most are concerned with whether magnetic ordering occurs, the ordering temperature, and the type of ordering, ferromagnetic, antiferromagnetic, etc. Contrary results have been reported.

To stabilize fcc Fe at low temperatures the following three methods have been developed: (1) the γ phase is extended by alloying Fe with Ni and Cr, as in the austenitic stainless steels, (2) coherent γ-Fe precipitates are formed in supersaturated Fe-Cu alloys, and (3) thin iron films are prepared by epitaxial growth on fcc substrates, such as single-crystal Cu surfaces.

It seems to be established that fcc Fe in austenitic steels and as precipitates in a Cu matrix are antiferromagnets with Néel temperatures of about 40 and 67 K, respectively.[4] The ordering temperature depends on composition, any alloying, and particle size. The atomic magnetic moments are small, about $0.7\mu_B$, and therefore correspond to a low-spin state. In recent work on Fe-Ni (Invar) alloys, however, it is reported that two distinct fcc-Fe phases can be present, one with high spin ($\sim 2.8\mu_B$) and ferromagnetically ordered below ~500 K, called the γ phase, and the other with low spin ($\sim 0.5\mu_B$) and antiferromagnetically ordered below ~20 K,[5] called the γ' phase.

For epitaxial fcc-Fe films, mainly on Cu substrates, a number of contrary results have been reported. By using macroscopic methods, fcc-Fe films on (011) and (111) surfaces were found to be ferromagnetic at room temperature.[6] On the other hand, Mössbauer spectroscopy indicated that the (100), (110), and (111) fcc-Fe films are paramagnets at room temperature and antiferromagnets below $T_N \simeq 80$ K.[7] In a polarized neutron experiment, no in-plane ferromagnetism was detected in (100) films at room temperature.[8] For epitaxial films of a few monolayers, both paramagnetic[9] and ferromagnetic[10] ordering at room temperature have been reported. Recently, conversion-electron Mössbauer spectra, obtained *in situ* in ultrahigh vacuum, of (100) fcc-Fe films from 10 to 17 monolayers thick implied antiferromagnetic ordering at $T_N \simeq 65$ K and, apparently, low-spin atomic moments.[11] It seems that the magnetic properties of fcc-Fe films depend critically on the lattice parameter, on chemical bonding with the substrate, and possibly on the preparation method and on the film orientation.

A number of theoretical calculations, based on band-structure methods, have attempted to determine the magnetic ground state of fcc Fe.[12] The energy of nonmagnetic (no polarization), low- and high-spin ferromagnetic and antiferromagnetic states has been determined as a function of the volume. It is found that the ground state depends sensitively on this volume so that phase transitions may occur when the experimental conditions are changed.

In view of the diversity of the experimental data and sensitivity of the theoretical results on the models used, it is clearly important to investigate fcc Fe in an isolated state. Then effects related to the substrate, matrix, and foreign-element interactions would be excluded. An early indication that this might be achievable was the discovery that in a conventional gas-evaporation (black smoke) technique some fine particles of fcc Fe are formed.[13] Unfortunately the great majority of the particles were bcc α iron. Later this method was upgraded and a higher yield, about 10% of the deposited particles, was obtained.[14] More recently, Majima (one of the current authors) *et al.*[15] synthesized fcc-Fe particles using a new laser technique and obtained a relatively high yield. These particles are the subject matter of this current investigation.

PARTICLE PREPARATION AND CHARACTERIZATION

A TEA (transversely excited atmospheric) CO_2 laser induced the dielectric breakdown, or, more precisely, the SF_6-sensitized infrared photodecomposition, of iron pentacarbonyl, $Fe(CO)_5$.[16] The carbonyl decomposition mechanism has now been clarified.[15,16]

A transmission-electron-microscope photograph of the particles obtained is shown in Fig. 1. It reveals the presence of very fine particles with a fairly uniform size distribution lying in the range from 6.5 to 8.5 nm; the mean particle size is ~8.0 nm.

In the x-ray diffractometer scan, as shown in Fig. 2, pronounced lines occur at $d=2.087$, 1.807, and 1.277.

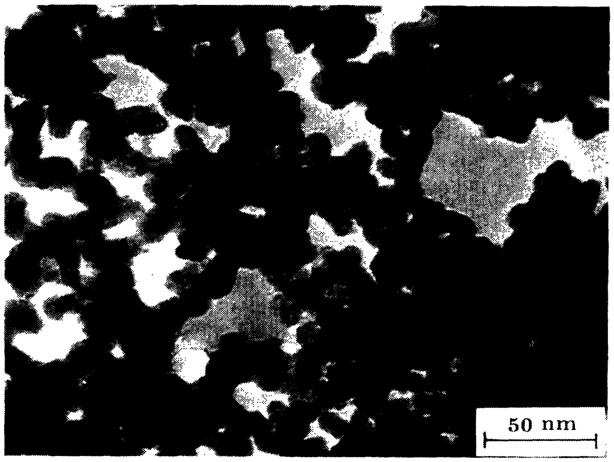

FIG. 1. Electron photomicrograph of nanometer-size particles (the Fe system) prepared by TEA CO_2 laser-induced breakdown of $Fe(CO)_5$.

These are consistent with reflections at (111), (200), and (220) planes, respectively, of the fcc structure of austenite. In addition, diffraction lines corresponding to α iron and a cubic iron oxide phase, either Fe_3O_4 or/and γ-Fe_2O_3, are observed with relatively high intensities. From these results and knowledge of the decomposition process of $Fe(CO)_5$,[15] the ultrafine particles can be reasonably assigned to a mixture of metallic iron with the fcc structure and with the bcc structure. Furthermore, it is well known that small metallic iron particles are sensitive to oxidation; indeed the presence of these iron oxides on the surface is essential in order to passivate these metallic particles.[17]

Since iron takes the fcc structure in the temperature range 1182–1662 K, it can be inferred that the particles with the fcc structural phase have originally been formed in this temperature range. Some of the particles, presumably the ultrafine particles, are cooled quickly enough to room temperature to retain the fcc structure, while the relatively large particles are cooled more slowly and then may have more likelihood to be transformed to the stable bcc phase. Another possibility is that the surface layers

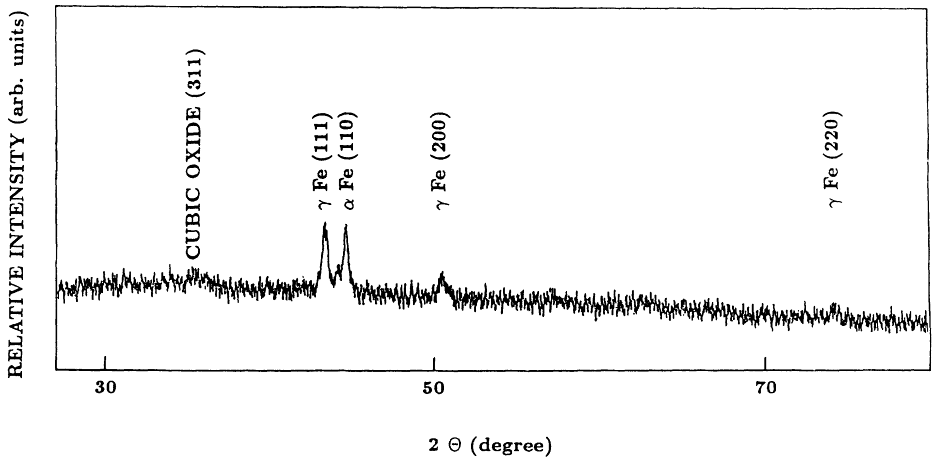

FIG. 2. X-ray diffraction pattern taken using Cu $K\alpha$ radiation of the nanometer-size particles (Fe system). Here 2θ is twice the Bragg angle.

of the particles are cooled quickly enough to retain the fcc structure and the inner cores of the particles are cooled more slowly and are transformed to the bcc structure. Judging from the remarkably uniform particle size (Fig. 1) the latter situation is perhaps more likely, although the possibility that the former scenario applies cannot be ruled out, and vice versa.

Mössbauer spectra over a large velocity scale, ±12.0 mm/s, were obtained between 1.8 K and room temperature. The source was ^{57}Co in a rhodium host. The spectra were collected with a Wissel multichannel analyzer controlled by an IBM XT. In order to search for any evidence of magnetic ordering in the fcc-Fe phase, Mössbauer spectra were also taken over a small velocity scale, ±2.0 mm/s. In addition, spectra were collected with a magnetic field applied parallel to the propagation direction of the γ ray. Since a sinusoidal drive mode was used, the data were folded and then fitted with subpatterns using a least-squares computer program.

RESULTS AND DISCUSSION

Typical Mössbauer spectra at the large velocity scale (±12.0 mm/s) at different temperatures are shown in Fig. 3. They confirm the x-ray diffraction data that in the preparation of fcc-Fe particles a certain amount of α-Fe and iron oxide phases is present.

A sextet subpattern with narrow linewidths that appears at every temperature has hyperfine fields H_{hf} almost exactly equal to the values observed for bulk α-Fe.[18] Since there is no indication of a diminished value even at room temperature, it is unlikely that any of the α-Fe particles are superparamagnetic.

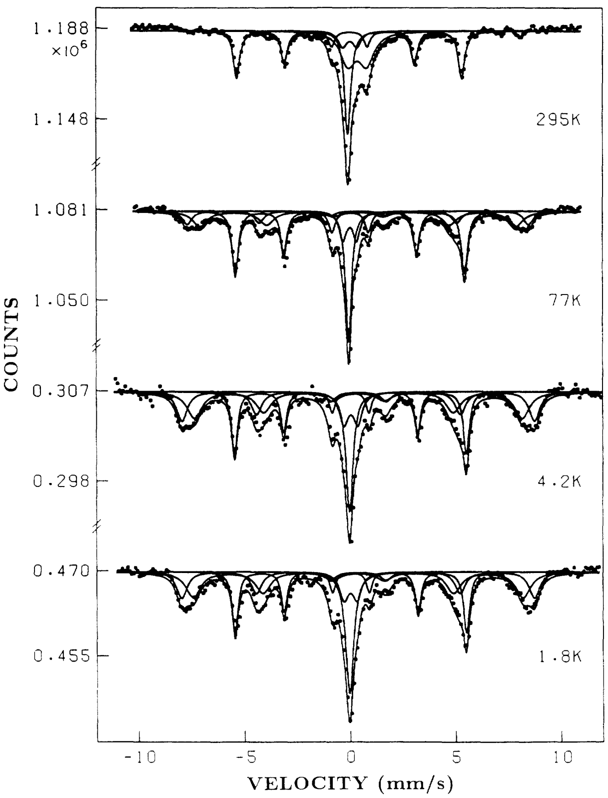

FIG. 3. ^{57}Fe Mössbauer spectra of the nanometer-size particles (Fe system) at various temperatures. The dots represent the data and the solid lines the subspectra as fitted by computer.

The iron oxide component is not magnetically split at room temperature. This feature is characteristic of the particle morphology that develops during a slow-oxidization mode; the origin is both a diminished recoilless fraction and superparamagnetism.[19] Because the linewidth associated with the iron oxides are broad at and below 77 K, two overlapping sextet patterns were fitted; at room temperature a doublet only was used. It is uncertain whether the iron oxides are Fe_3O_4, γ-Fe_2O_3, or a mixture.

For the fcc-Fe phase, one singlet and one doublet were required for a satisfactory spectral fit. The central singlet can be attributed to a fcc-Fe phase in which each iron atom has 12 nearest-neighboring Fe atoms as in the bulk; then the quadrupole interaction will be zero. A doublet has been used before for ultrathin fcc-Fe films grown epitaxially on copper; this subpattern was attributed to the fcc-Fe layer at the Cu interface.[11] A similar origin is suggested here, that is, the doublet corresponds to iron atoms at the surface or interface between the fcc-Fe phase and the iron oxide or α-Fe phases where the number of nearest Fe atoms is different. This lack of local cubic symmetry at the iron sites will lead to a nonzero electric-field gradient (EFG).

The computer fits for the subspectra are also shown in Fig. 3 and the corresponding hyperfine parameters are listed in Table I. In order to infer the relative amounts of each phase from the areas of the subpatterns, only spectra at temperatures near 4.2 K should be used in order to eliminate as far as possible Mössbauer recoilless fraction and superparamagnetic variations. Then, the relative amounts of fcc Fe, α-Fe, and iron oxides deduced are 25, 25, and 50 at. %, respectively. In similar measurements made on the same sample about two years earlier, the corresponding amounts found were 30, 25, and 45 at. %, respectively, that is, the fcc Fe phase decreased by 5 at. % and the iron oxide increased by 5 at. %. This implies that the fcc Fe has oxidized slightly with time and suggests a composite particle structure. To be specific, the core of the particle is the α-Fe phase formed during a slower cooling rate than for the surface during the formation process. On slow oxidization the surface layer becomes the iron oxide and the middle layer in between is the fcc-Fe phase.

Contrary to many previous reports for fcc-Fe precipitates or films, no line broadening, which could indicate the onset of magnetic ordering, is observed for this phase in the spectra of Fig. 3, even at 1.8 K. In order to make a more accurate examination, Mössbauer spectra were collected over a velocity scale of ±2.00 mm/s; they are shown in Fig. 4 for several temperatures. Subspectra corresponding to those used to fit the large velocity scale and constrained to have the same area ratios were fitted by computer. These are also shown (as full curves) in Fig. 4. For the α-Fe pattern, only lines 3 and 4 appear. For the iron oxides, lines 3 and 4 for each of the poorly resolved

TABLE I. Parameters deduced from the Mössbauer spectra, velocity range ±12.0 mm/s. Here H_{hf} is the hyperfine field in kOe, ε, δ, and Γ are the quadrupole splitting, isomer shift with reference to an α-Fe foil, and linewidth (full width at half maximum), respectively, all in mm/s. The proposed phase identification and their areas in relative percent are also given.

T (K)	Phase	H_{hf}	ε	δ	Γ	Area
295	α-Fe	330	0	0	0.36	34
	Fe oxides		0.90	0.35	0.85	37
	fcc Fe			−0.088	0.35	18
			0.67	0.008	0.50	11
77	α-Fe	336	0	0	0.36	36
	Fe oxides	463	0	0.38	0.85	24
		501	0	0.38	0.54	13
	fcc Fe			−0.052	0.35	18
			0.65	0.002	0.42	9
4.2	α-Fe	340	0	0	0.36	25
	Fe oxides	481	0	0.39	0.85	28
		517	0	0.39	0.60	22
	fcc Fe			−0.032	0.40	15
			0.66	0.024	0.52	10
1.8	α-Fe	340	0	0	0.34	25
	Fe oxides	484	0	0.37	0.85	29
		518	0	0.37	0.60	21
	fcc Fe			−0.048	0.45	17
			0.61	−0.004	0.52	8

subpatterns are drawn for the spectra at 77 K and below and one doublet for room temperature. For the fcc Fe a doublet and a singlet are used. The hyperfine parameters deduced from the fitting are listed in Table II. In contrast to the spectra of Fig. 3 where the source was always at room temperature, for the spectra of Fig. 4 in the liquid-helium region, the source was also cooled to 4.2 K. As a result a small broadening of about 0.02 mm/s occurred in the source. Then, in view of fitting errors, possible vibration of the spectrometer, and source broadening, the broadening in the fcc-Fe singlet is probably zero. However, at most this broadening is 0.05 mm/s which corresponds to a hyperfine field of about 1.5 kOe (0.15 T).

In order to pursue this topic further, Mössbauer spectra were taken over the small velocity range of ±2.0 mm/s with a magnetic field of 50 kOe (5.0 T) applied parallel to the propagation direction of the γ ray; they are shown in Fig. 5 for temperatures of 1.8, 4.2, and 20

TABLE II. Mössbauer parameters for nanometer-size particles (Fe system), velocity range ±2.0 mm/s.

T (K)	Phase	H_{hf}	ε	δ	Γ	A
77	α-Fe	336	0	0	0.28	16
	Fe oxides	463	0	0.44	0.64	12
		501	0	0.44	0.35	7
	fcc Fe			0.008	0.30	46
			0.67	0.05	0.27	19
10	α-Fe	340	0	0	0.30	13
	Fe oxides	480	0	0.42	0.66	13
		516	0	0.42	0.52	9
	fcc Fe			−0.01	0.30	45
			0.66	0.04	0.28	20
4.2	α-Fe	340	0	0	0.30	12
	Fe oxides	480	0	0.45	0.61	14
		517	0	0.45	0.47	8
	fcc-Fe			−0.07	0.35	46
			0.65	0.06	0.34	20
1.8	α-Fe	340	0	0	0.30	12
	Fe oxides	485	0	0.49	0.66	15
		518	0	0.49	0.45	8
	fcc Fe			−0.01	0.40	47
			0.65	0.05	0.36	18

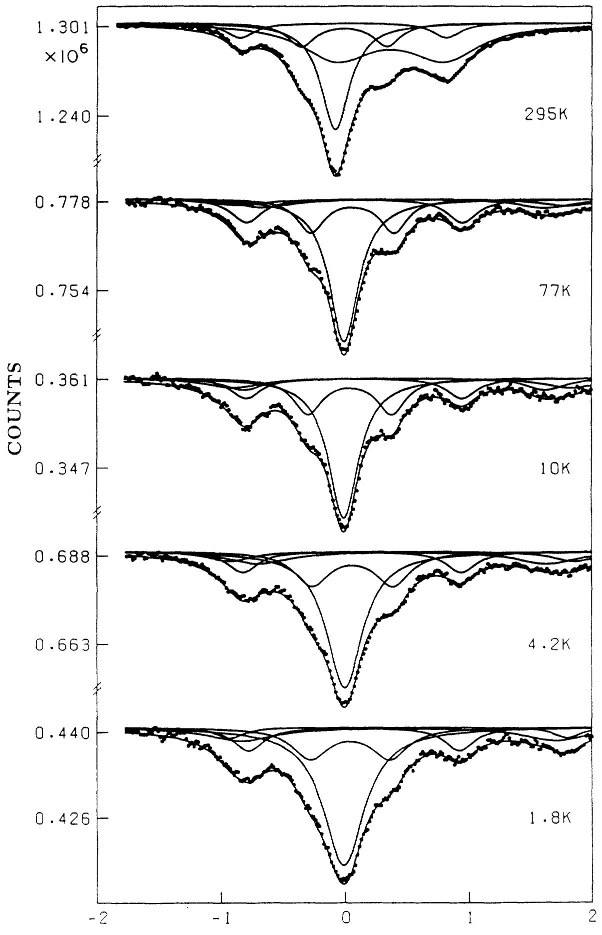

FIG. 4. ^{57}Fe Mössbauer spectra over a ±2.0 mm/s velocity range of the nanometer-size particles for various temperatures. Both the data and computer fittings are shown.

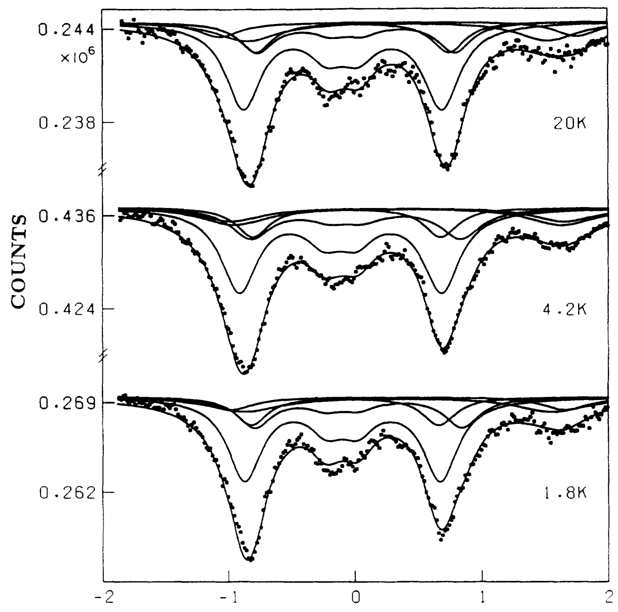

FIG. 5. ^{57}Fe Mössbauer spectra at various temperatures over a ±2.0 mm/s velocity range with a magnetic field of 50 kOe (5 T) applied parallel to the propagation direction of the γ ray.

K. Good fits were obtained by replacing the original singlet and doublet assigned to the fcc-Fe phase by two four-line patterns, which are actually sextet patterns with zero absorption areas for the second and fifth lines. It is well known that when the magnetization, hence also the hyperfine field, is along the γ-ray direction, the second and fifth lines will be absent because of a selection rule. This situation will occur for a paramagnet, illustrated by the spectra of dilute ^{57}Fe in metallic Ti at room tempera-

TABLE III. Mössbauer parameters for Fe system in a 50-kOe external magnetic field, velocity scale ±2.0 mm/s.

T (K)	Phase	H_{hf}	δ	Γ	A
20	α-Fe	295	0	0.32	12
	Fe oxides	476	0.34	0.59	14
		533	0.34	0.42	8
	fcc Fe	48.5	−0.09	0.35	50
		48.3	−0.02	0.33	16
4.2	α-Fe	296	0	0.32	11
	Fe oxides	477	0.35	0.65	13
		528	0.35	0.60	10
	fcc Fe	49.4	−0.12	0.35	48
		51.2	0.03	0.39	18
1.8	α-Fe	296	0	0.32	12
	Fe oxides	475	0.32	0.70	14
		528	0.32	0.45	8
	fcc Fe	48.8	−0.10	0.33	48
		50.6	−0.04	0.34	18

ture in a 100-kOe field[20] or of fcc-Fe precipitates in Cu at 78 K in a 50-kOe field,[21] for a ferromagnet, for most ferrimagnets, but not for an antiferromagnet. Indeed, a fit with a sextet could not be found, which is additional evidence that antiferromagnetic ordering of the fcc-Fe particles does not occur.

The hyperfine parameters obtained from fitting the spectra of Fig. 5 are listed in Table III. Of particular interest are the hyperfine fields for the fcc-Fe subspectra. They are close to but not exactly equal to the applied field, 50 kOe. It should be recalled that there can be other contributions to the hyperfine field even for a paramagnet; these include a demagnetization term, a Lorentz term, and perhaps vacancy, surface, or interfacial contributions. Incidentally, any argument that the fcc-Fe phase is superparamagnetic can also be discarded on the basis of the in-field spectra. It then appears that the nanometer fcc-Fe particles are either just paramagnets or at most possess a hyperfine field at 1.5 kOe or less when no external field is applied at least down to 1.8 K.

In view of the surprising result that nanometer particles of fcc iron have magnetic properties that differ from fcc-iron alloys, precipitates, or thin films, a literature search was conducted to see if any hint of this behavior had been observed previously; two interesting papers have been found. In one, Victorian (Australian) brown coal was reduced by heating and studied by Mössbauer spectroscopy at room temperature and at 4.2 K using a ±12.0 mm/s velocity range.[22] A central singlet, argued to be a γ-Fe pattern, broadened only by about 0.10 mm/s between these two temperatures, suggesting paramagnetism at low temperatures. A doublet was also fitted; it was thought to be γ-Fe with one nearest-neighbor carbon atom (from the coal). Although there is no evidence that any carbon remains after the decomposition of the iron pentacarbonyl in the fcc-Fe particles in this current study, this possibility cannot be ruled out. In the second paper, Mössbauer spectra were obtained over the ±12.0 mm/s velocity range for ultrafine iron particles made by gas evaporation.[23] A singlet, about 4% or 5% of the total absorption area, had a linewidth that decreased about 0.09 mm/s when the temperature was lowered from 100 to 4.2 K. This subspectrum was identified as nanometer fcc Fe that remained paramagnetic down to 4.2 K. Of course, the other overlapping patterns and the small amount of the fcc-Fe phase present made an unambiguous conclusion difficult. Nevertheless, the results of the brown coal and the gas-evaporation nanometer-size iron particles agree and support the conclusion in this present study.

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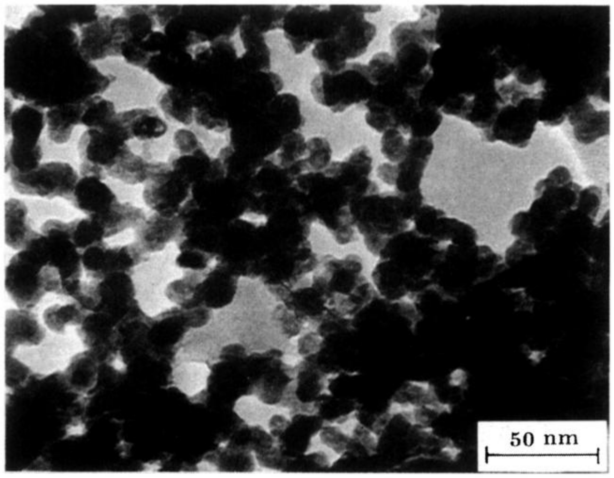

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