

# Electron microscopy and Mössbauer study of superlattices in iron films

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Annealing iron films grown by a pulsed vacuum technique gives rise to a superlattice. Mössbauer studies show that a new electronic and magnetic state of iron arises in the process. © 1995 American Institute of Physics.

Structural modifications which lead to the formation of large-period superlattices have been observed in several materials which display a tendency toward polymorphic transitions. This effect was studied in AuMn alloys in detail in Refs. 1 and 2. Sato *et al.* suggest that the change in the structure of these alloys as their composition is varied is similar to the polytypism observed in SiC single crystals.<sup>3</sup> Despite the superficial similarity between these effects, however, the formation of the superlattices in the different materials differs in nature. While the onset of polytypism in SiC depends on the crystal growth mechanism, in metal alloys the conduction electrons play an important role in shaping the superlattice. At the same time, the difference between the structures of superlattices in metal alloys in bulk and film samples shows that the mechanisms for the formation of long-period structures are far from being fully understood.<sup>2</sup>

In this letter we are reporting a study of a superlattice observed in Fe films. The technique for growing the films is described in Ref. 4; their thickness was  $\sim 500$  Å. We studied the changes in the structure and magnetic properties of the samples during multistage annealing over the temperature range 100–800 °C in a vacuum of  $10^{-5}$  torr. The duration of the annealing stage at each fixed temperature was 1 h. Figure 1 shows some electron-microscopy results. In its initial state, the film is x-ray-amorphous. The diffraction pattern consists of a diffuse halo (Fig. 1a). After annealing at  $T=200$  °C, crystallization begins (Fig. 1b): Against the background of the halo, some reflections corresponding to the  $\alpha$  and  $\gamma$  phases of iron arise. The lattice constant of the  $\alpha$  phase is  $a=2.86$  Å, and that of the  $\gamma$  phase  $a=3.57$  Å. A further annealing intensifies the contributions of these phases, while the electron diffraction pattern acquires reflections from a superlattice in addition to those from the  $\alpha$  and  $\gamma$  phases. The microstructure of the film is a network of dendrites growing away from crystallization centers. Figure 1c shows a typical electron diffraction pattern recorded from one branch of a dendrite ( $T_{\text{ann}}=400$  °C). The electron microscopy revealed that the different branches of a dendrite are oriented in a coherent fashion. The reflections from  $\gamma$ -Fe and the superlattice disappear at  $T_{\text{ann}}=700$  °C, and the sample is left with only polycrystalline  $\alpha$ -Fe (Fig. 1d).

Figure 2a illustrates the indexing of the electron diffraction pattern in Fig. 1c. The filled circles are reflections of  $\gamma$ -Fe, the open circles are reflections of the superlattice,

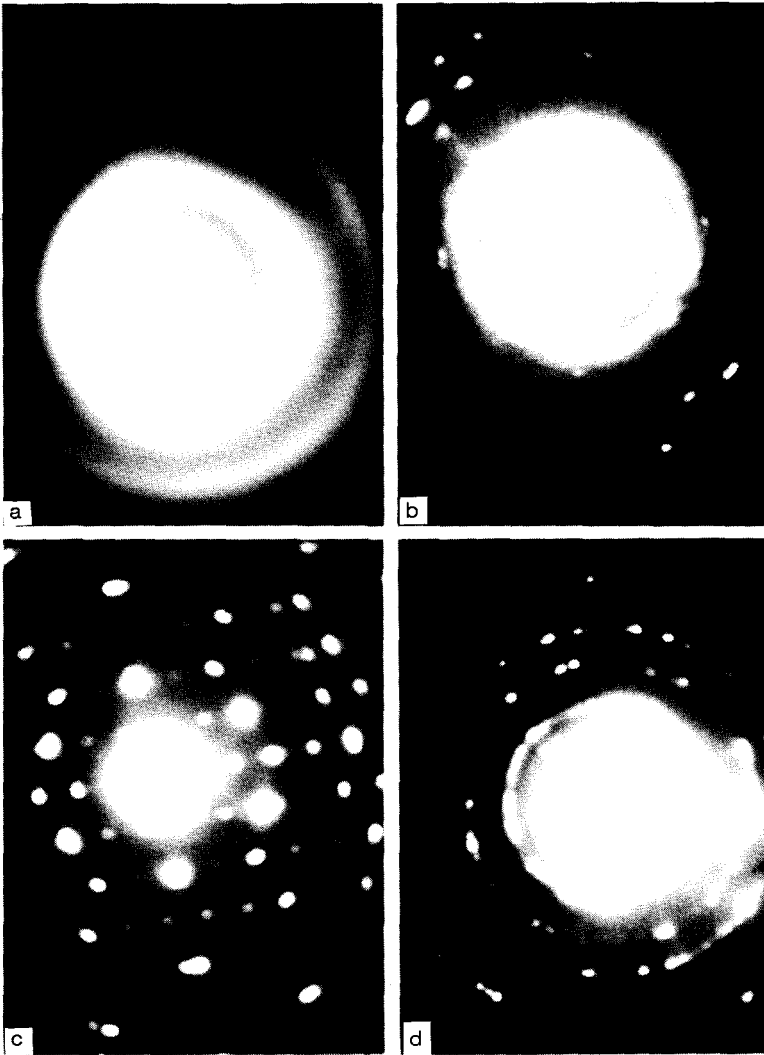


FIG. 1. Electron diffraction patterns for Fe films. a—Original state; b— $T_{ann}=200$  °C; c—400 °C; d—700 °C.

and the double circles are reflections of  $\alpha$ -Fe. The crosses are double-diffraction effects. The reciprocal-lattice vectors of the superlattice are

$$\bar{g}_1 = \frac{1}{5d_{211(\alpha\text{-Fe})}}, \quad \bar{g}_2 = \frac{1}{5d_{222(\alpha\text{-Fe})}},$$

where  $d_{211}$  and  $d_{222}$  are the distances between the corresponding atomic planes (Fig. 2a). The corresponding constants of the superlattice are  $a = 5.80$  and  $c = 4.32$  Å.

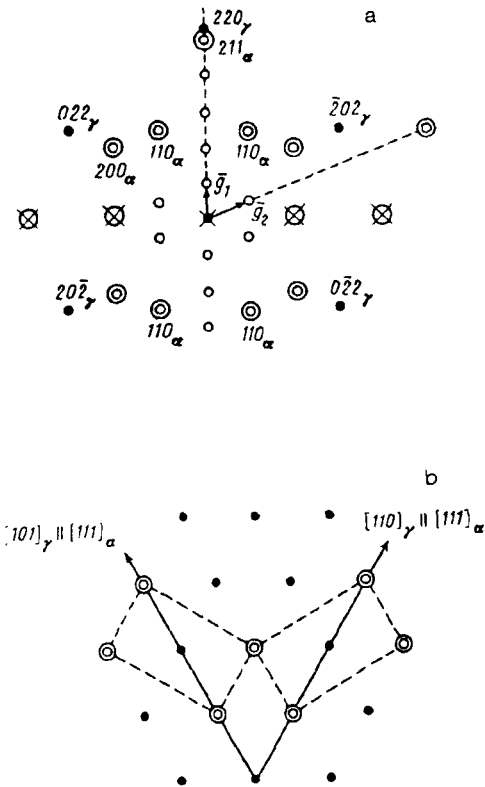


FIG. 2. a: Indexing of the electron-diffraction pattern in Fig. 1c. Filled circles—Reflections of the  $\gamma$  phase; double circles—reflections of the  $\alpha$  phase; circles with crosses—double diffraction; open circles—reflections from the superlattice. b: schematic diagram of  $\alpha$ -Fe twins (dashed lines) in the (111) plane of  $\gamma$ -Fe, which are related by Kurdyumov-Zaks orientation relation (1). Filled circles—Atoms of  $\gamma$ -Fe; double circles—atoms of  $\alpha$ -Fe.

An indexing of the electron diffraction patterns shows that the superlattice forms through a strict alternation of the  $\gamma$ -Fe phase and  $\alpha$ -Fe twins which satisfy the Kurdyumov-Zaks orientation relations

$$(111)[011]_{\gamma\text{-Fe}} \parallel (110)[111]_{\alpha\text{-Fe}}, \quad (111)[101]_{\gamma\text{-Fe}} \parallel (110)\{111\}_{\alpha\text{-Fe}}. \quad (1)$$

These relations are written for  $\alpha$ -Fe twins with a (211) twinning plane (Fig. 2b). The electron-microscopy data currently available are an insufficient basis for constructing a complete picture of the alternation of the  $\gamma$ -Fe phases and the  $\alpha$ -Fe twins in the superlattice. It can nevertheless be suggested that the very nonequilibrium conditions under which the crystalline phase forms in our case<sup>5</sup> may be the reason for the stabilization of the high-temperature  $\gamma$ -Fe phase at room temperature.

The magnetization of the test films was measured on an induction magnetometer. In the original state we found  $M_s \approx 1100$  G. This figure remained essentially constant in the face of annealing at temperatures  $T_{\text{ann}} < 700$  °C. After annealing at  $T_{\text{ann}} > 700$  °C, the magnetization rose to  $\sim 1700$  G. That figure corresponds to the saturation magnetization of pure  $\alpha$ -Fe.

Mössbauer spectra were measured for films doped with the isotope  $\text{Fe}^{57}$ . We used a  $\text{Co}^{57}(\text{Cr})$  source at room temperature (Fig. 3). The spectral lines of the original film are very broad and develop on a trough-shaped base, as is typical of ultradisperse and amor-

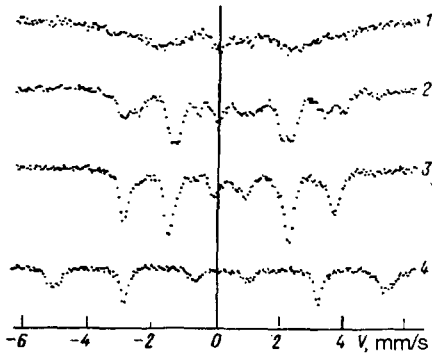


FIG. 3. Mössbauer spectra of a Fe film. 1—Original state; 2— $T_{\text{ann}}=200^\circ\text{C}$ ; 3— $400^\circ\text{C}$ ; 5— $700^\circ\text{C}$ .

phous states. In the course of the annealing, the spectral lines thicken, and the spectra themselves can be approximated satisfactorily by Zeeman sextets with the parameter values listed in Table I.

The trough-shaped base of the spectra is probably caused by iron atoms in remaining amorphous regions, whose volume decreases in the course of the annealing. As the annealing temperature is raised, the populations of the positions characterized by sextet 2 decreases. After the final annealing at  $700^\circ\text{C}$ , the entire film is in a state for which the parameters of the hyperfine structure of the spectra are approximately the same as those of  $\alpha\text{-Fe}$ .

The parameters of sextets 1 and 2 (i.e., the hyperfine fields and the chemical shifts) are approximately the same as the corresponding parameters of the spectra of Fe-C alloys<sup>6</sup> having an hcp structure. However, x-ray photoelectron spectroscopy reveals that the carbon content in our films is no more than 3 at. %, and the concentration of bound carbon is even lower. Furthermore, we did not observe the decomposition products which we would expect in the case of an annealing of Fe-C alloys. The spectra of our films do not contain the single paramagnetic line characteristic of fcc  $\gamma\text{-Fe}$ .

TABLE I. Parameters of the hyperfine structure of the Mössbauer spectra of the iron films.

	After annealing at $200^\circ\text{C}$		After annealing at $400^\circ\text{C}$		After annealing at $700^\circ\text{C}$
	Sextet 1	Sextet 2	Sextet 1	Sextet 2	
$H_{\text{st}}$	211	182	207	179	333
$\delta$	0.24	0.19	0.19	0.18	0.01
$\epsilon$	+0.01	0	0	-0.02	0.01
$\Gamma$	0.30	0.29	0.33	0.34	0.29
$S$	29	32	73	14	100
$S_t$	39		13		-

$H_{\text{st}}$  is the field at the  $\text{Fe}^{57}$  nucleus ( $\pm 5$  kOe);  $\delta$  is the chemical isomer shift with respect to  $\alpha\text{-Fe}$  ( $\pm 0.03$  mm/s);  $\epsilon$  is the quadrupole splitting estimated from the positions of outer lines,  $(V_6 - V_5 - V_2 + V_1)/4$  ( $\pm 0.03$  mm/s);  $\Gamma$  is the linewidth at half-maximum ( $\pm 0.03$  mm/s);  $S$  is the area of the partial spectrum ( $\pm 5\%$ ); and  $S_t$  is the area of the trough-shaped base of the spectrum ( $\pm 5\%$ ).

The Mössbauer spectra suggest that a new electronic and magnetic state of iron characterized by  $H_{st} \approx 207$  kOe and  $\delta \approx 0.19$  mm/s forms during the synthesis and annealing of these films.

Taken together, the results on the electron diffraction (the coexistence of reflections characteristic of the  $\alpha$  and  $\gamma$  phases of iron along with superreflections) and on Mössbauer spectroscopy (a sextet with parameters different from those of the  $\alpha$  and  $\gamma$  phases of iron) can be explained by assuming that there are alternating lattices of  $\alpha$ -Fe and  $\gamma$ -Fe with approximately equal interatomic distances which satisfy the Kurdjumov–Zaks orientation relations.

In a structure of this type we might expect changes in the effective coordination number of the iron atom from those characteristic of  $\alpha$ -Fe (8) and  $\gamma$ -Fe (12). Ideally, we might encounter coordination numbers of 9, 10, and 11 in a superstructure of this sort. Changes in the electronic state of the iron atom with changes in coordination number lead to the observed Mössbauer results.

We attribute the formation of the superlattice in these samples both to particular features of the original structure, which high-resolution electron microscopy describes as a set of microscopic clusters 20–30 Å in size, and to the particular features of the process by which these films crystallize.<sup>5</sup>

<sup>1</sup>H. Sato and R. S. Toth, *J. Phys. Chem. Solids* **27**, 28 (1966).

<sup>2</sup>H. Sato *et al.*, *J. Phys. Chem. Solids* **28**, 137 (1967).

<sup>3</sup>A. R. Verma and P. Krishna, *Polymorphism and Polytypism in Crystals* (Wiley, New York, 1966).

<sup>4</sup>G. I. Frolov *et al.*, *Fiz. Tverd. Tela* (Leningrad) **36**, 970 (1994) [*Phys. Solid State* **36**, 526 (1994)].

<sup>5</sup>V. G. Myagkov *et al.*, *Poverkhnost'* **1**, 105 (1994).

<sup>6</sup>H. Berners *et al.*, *J. Phys. Chem. Solids* **28**, 17 (1967).

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