BRIEF COMMUNICATIONS

On the γ-Fe$_2$O$_3$ Superstructure Observation by High Resolution Electron Microscopy

GALINA N. KRYUKOVA, ANDREI L. CHUVILIN,
AND VLADISLAV A. SADYKOV[1]

*Institute of Catalysis, Siberian Branch of the USSR Academy of Sciences,
Prospekt Akademika Lavrentieva 5, Novosibirsk 630090, USSR*

A pronounced development of the superstructure in slightly reduced γ-Fe$_2$O$_3$ particles has been observed with the aid of high resolution electron microscopy. The model of superstructure formation as a result of vacancy ordering has been proposed on the basis of computer simulation images. Twins of the (110) type have also been detected. © 1990 Academic Press, Inc.

γ-Fe$_2$O$_3$ is well-known to be a component of some catalysts for selective oxidation reactions (*1*). It is widely used in magnetic recording media. There is a suggestion that the reactivity (*2*) and magnetic properties (*3*) of γ-Fe$_2$O$_3$ may be attributed to the real structure of their particles. However, little is known in detail about the defect structure versus the stoichiometry of this material.

According to Ref. (*4*) the basic structure of γ-Fe$_2$O$_3$ is closely related to that of the inverse spinel Fe$_3$O$_4$ with a statistical distribution or regular ordering of the octahedral cation vacancies. These data, obtained with the aid of X-ray powder diffractometry (*5*) and the neutron diffraction method (*6*), correspond to mean values and therefore are not reliable. This method of high resolution electron microscopy (HREM) has made possible direct imaging of the atomic structure of solids. We report here on HREM

studies of the γ-Fe$_2$O$_3$ structure. The instrument used for work described below was a transmission electron microscope JEM-100B with a specially constructed top entry specimen stage and an objective lens with spherical aberration $C_s = 1.2$ mm. The instrumental resolution of this machine operated at an accelerating potential of 100 kV approaches 3 Å.

The specimen of γ-Fe$_2$O$_3$ was prepared from acicular spinel Fe$_3$O$_4$ (the starting material was α-FeOOH) by its oxidation in O$_2$ at low (~250°C) temperature. The as-prepared sample was then reduced in microreactor to the stoichiometry Fe$_2$O$_{2.97}$ by pulses of 0.3% CO in He at 227°C or by the treatment at 400°C in He (oxygen admixture ~5 ppm). Both as-prepared and reduced specimens were identified as γ-Fe$_2$O$_3$ by X-ray powder diffraction method.

Figure 1 shows a bright field image of the as-prepared particles viewed down the [110] direction. A corresponding electron diffrac-

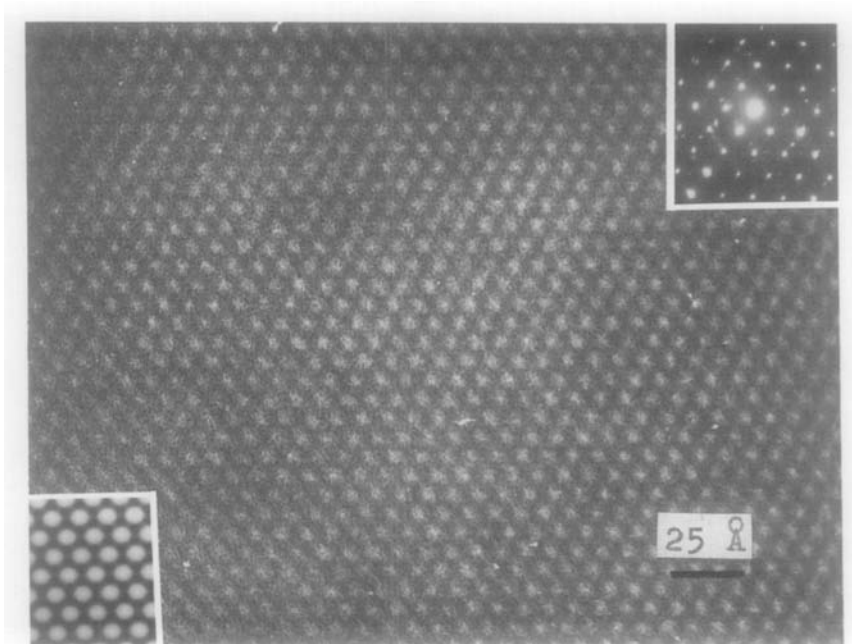[1] To whom correspondence should be addressed.

FIG. 1. High-resolution micrograph of as-prepared sample of γ-Fe_2O_3 oriented into [110] zone axis. A corresponding electron diffraction pattern is situated at the top. Computer image based on idealized Fe_3O_4 is included in the micrograph (see text for further discussion).

tion pattern is situated in the inset. No difference in the HREM images of as-prepared specimen and spinel is observed, as seen from computer simulation image based on Fe_3O_4, which is included in Fig. 1. Therefore a statistical distribution of cation vacancies seems to be obtained for stoichiometric γ-Fe_2O_3. A space group of this specimen appears to be *Fmmm*.

By inspection of the micrograph of the reduced sample (Fig. 2) one can see a pronounced development of superstructure along the **a** axis with a period equal to $3a$. The crystal is oriented into the same zone axis as in Fig. 1, i.e., [110]. The electron diffraction pattern is shown at the top of the micrograph. We have proposed a model of superstructure formation based on the ordering of Fe vacancies distributed on octahedral and tetrahedral sites in the spinel lattice with a threefold unit cell along a axis. This model was used for image calculations

based on the multislice method. Such computer simulation image fits in with the experimental micrograph (see inset in Fig. 2). Other models based on statistical or ordered distribution of octrahedral vacancies only were not in good accord with experimental observations. Though no space group could be derived from the bidimensional diffraction patterns our results indicate that nonstoichiometric γ-Fe_2O_{3-x} possesses a tetragonal unit cell.

Thus, the data gained in the present investigation show the superstructure development in γ-Fe_2O_3-reduced specimens. Besides the superlattice, several features of the structural arrangement are also evident from the micrographs. For example, the arrow A in Fig. 3 indicates the crystal parts in a twin relationship. In this case the crystal is oriented along the [001] zone axis. The electron diffraction pattern (see inset in Fig. 3) shows that the twin plane is (110) type.
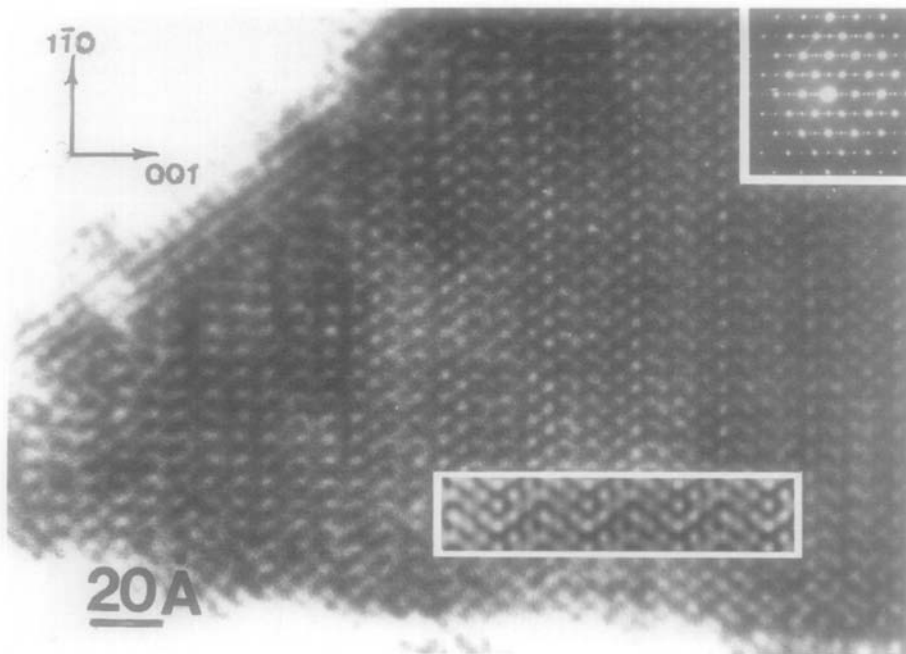
FIG. 2. The structure of the reduced γ-Fe$_2$O$_3$ particle imaged into [110] projection. There is a strong evidence of the formation of superstructure with a threefold unit cell.

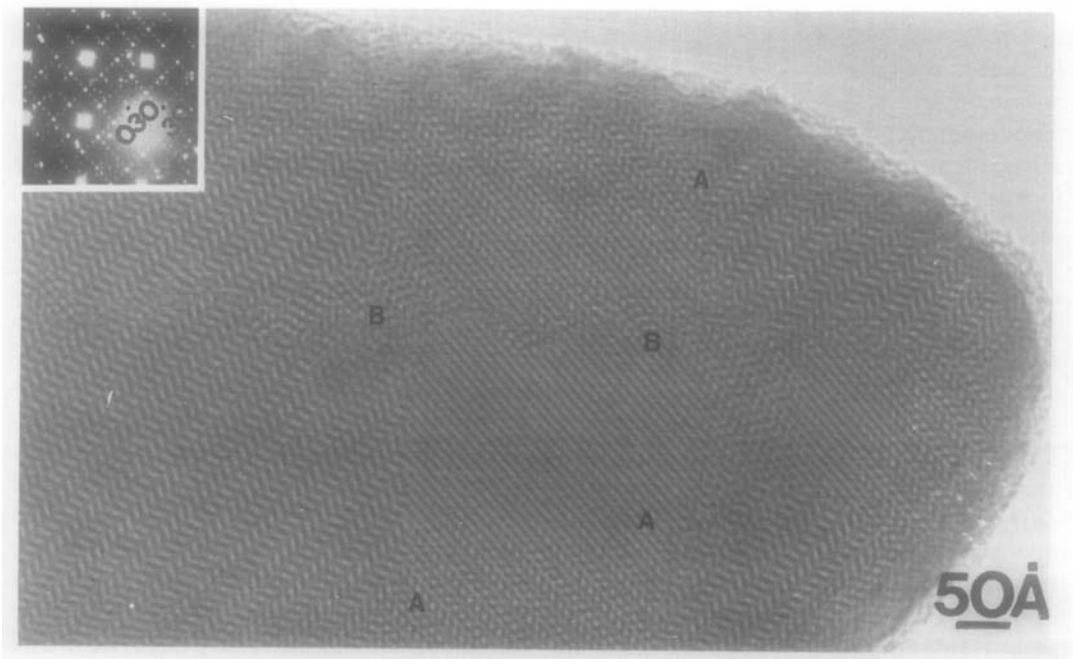FIG. 3. Micrograph of the reduced γ-Fe$_2$O$_3$ particle. Twin boundaries (A) and incoherent stacking of the crystalline blocks (B) are arrowed.

These twins are a prominent defect in reduced γ-Fe_2O_3 specimen. One can also see areas that approach incoherent stacking of the crystalline blocks (as shown by B).

The present observations are the first published HREM images of the structure of γ-Fe_2O_3 prepared from synthetic Fe_3O_4 crystals. This HREM study has revealed the presence of the superlattice and structural imperfection for γ-Fe_2O_3 specimens. According to Refs. (7 and 8) the high activity and selectivity of γ-Fe_2O_3 in oxidative dehydrogenation of butene appears to be associated with a possibility of an easy cation exchange between the bulk and the surface structure of the catalyst particles. The formation of superstructure and other extended defects in the structure of γ-Fe_2O_3 may promote such cation migration.

It seems also likely that our results can provide indispensable information for further improvement of the magnetic recording media based on γ-Fe_2O_3. Thus, saturation magnetization is a function of the cation distribution. Therefore, according to our data, this parameter will depend upon stoichiometry determined by processing conditions. The coercivity is influenced by the morphology and microstructure of the particles and will be greatly affected by twin boundaries normal to $\langle 110 \rangle$ easy axis of the material.

Acknowledgments

References

1. C. L. THOMAS, "Catalytic Processes and Proven Catalysts," Academic Press, New York (1970).
2. U. COLOMBO, F. GAZZARRINI, AND G. LANZAVECCHIA, *Mater. Sci. Eng.* **2**, 125 (1967).
3. G. BATE, "Ferromagnetic Materials," (E. P. Wohlfarth, Ed.), Vol. 2, p. 443 (1980).
4. G. W. OOSTERHOUT AND C. J. M. ROOIMANS, *Nature (London)* **181**, 44 (1958).
5. K. HANEDA AND A. H. MORRISH, *Solid State Commun.* **22**, 779 (1977).
6. C. GREAVES, *J. Solid State Chem.* **49**, 325 (1983).
7. K. SAKUTA, F. UEDA, M. MISONO, AND Y. YONEDA, *Bull. Chem. Soc. Japan* **53**, 324 (1980).
8. M. MISONO, K. SAKUTA, F. UEDA, Y. NOZAWA, AND Y. YONEDA, *Bull. Chem. Soc. Japan* **53**, 648 (1980).