Comment on "Magnetically Ordered fcc Structure at the Relaxed Grain Boundaries of Pure Nanocrystalline Fe"

Del Bianco *et al.* [1] report the formation of fcc Fe at the grain boundaries of bcc Fe in the 520–670 K temperature range during the grain growth process of the bcc phase in ball-milled iron powder. The presented experimental evidence is highly ambiguous and the unprecedented assumption is not supported by thermodynamic or kinetic considerations.

The hyperfine field distributions evaluated from the Mössbauer spectra [1] undoubtedly indicate the appearance of a component after annealing which has a 21 T hyperfine field, and the Curie temperature of this component is estimated to be about 500 K from the magnetization measurements [1]. However, the isomer shift of this component is about $+0.2$ mm/s as estimated from their Fig. 1, in contrast to the -0.09 mm/s value of the antiferromagnetic fcc Fe [2] which was extensively studied as precipitates in the Fe-Cu system. This large difference in the isomer shift is not mentioned in the paper. The value of the deduced hyperfine field also contradicts the theoretical predictions [3] and the few experimental observations [4] which indicate a higher hyperfine field of the ferromagnetic fcc phase observed in epitaxial films exclusively. The works referred to in Ref. [1], which yield 21–22 T hyperfine field, investigated equiatomic Fe-Cu solid solutions and clearly showed the approach to the well-known antiferromagnetic state (with no magnetic order at ambient temperature) as the Cu content was decreased by heat treatments. On the other hand, the average hyperfine field (20.6 T), the isomer shift (0.17 mm/s), and the Curie temperature (483 K) of Fe_3C [5] agree quite well with those of the component in question. Since carbon impurities are quite possible under ball milling conditions [6] and the formation of different Fe-C phases by solid state reaction has already been observed [7], the possibility that the phase appearing after heat treatment is Fe_3C should have been checked as well. Measuring the Mössbauer spectrum above the Curie temperature could have provided information on the quadrupole splitting which is expected to be zero in the case of cubic symmetry but has about a 0.4 mm/s average value in Fe_3C [5].

The presented selected area diffraction pattern [1] does not provide evidence for the presence of the fcc phase in the annealed sample. All of the spots in the diffraction pattern (including the encircled spots attributed to the fcc structure) can be indexed as the $\langle 111 \rangle$ zone of α-Fe. The diffraction rings starting from the inside correspond to the reflections: (110), (211), and (220). The observed lattice spacings are at 2.03, 1.17, and 1.015 Å, which correspond either to the (110), (211), and (220) reflections of the bcc structure or to the (111), (220), and (311) reflections of the fcc structure with lattice spacings 2.027, 1.170, and 1.013 Å and 2.026, 1.241, and 1.058 Å, respectively. The (200) reflection with the lattice spacings of 1.433 and 1.755 Å, respectively, which would in fact be decisive to differentiate between the bcc and the fcc structures is missing. This is attributed [1] to the special orientation of the grains. The problem of fcc or bcc indexing could have been solved showing two dark field images of the sample corresponding to the (311) (fcc notation) reflection and to the reflection at half of it [or (110) and (220) reflections in bcc notation]. If the fcc indexing is correct these reflections should belong to different grains. Further evidence could have been given by showing the x-ray diffraction pattern, where the (200) reflection should give a well-resolved contribution if about 5% fcc Fe phase were present, as inferred from the Mössbauer spectra.

In conclusion, neither the Mössbauer spectra nor the electron diffraction results presented prove adequately the claim that fcc Fe can be formed during the grain growth of pure nanocrystalline Fe. Care should always be taken to rule out the role of possible impurities when results contradicting the well-established observations in nonequilibrium systems are reported [8].

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