

Reply to “Comment on ‘Grain-boundary structure and magnetic behavior in nanocrystalline ball-milled iron’”

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In their Comment Balogh *et al.* criticize our paper [Phys. Rev. B **56**, 8894 (1997)] dealing with nanocrystalline Fe synthesized through ball milling by varying the duration of the milling process (2, 4, 8, 16, and 32 h) so to obtain powder with different mean grain size, in the 8–25 nm range. Balogh *et al.* suggest that it is possible to explain some features of the Mössbauer spectra of these powders, shown in the original paper, by impurities instead of the presence of a grain-boundary region among the crystallites. In particular, they claim that 0.3–0.5 at. % Cr, deriving from the milling process, is present in the sample milled for the longest time. In this reply, we discuss energy dispersive x-ray spectroscopy results demonstrating the absence of Cr, at least in an amount higher than 0.1 at. %. Moreover, we contest the statement that steel milling tools necessarily introduce significant levels of Cr impurity into the milled materials. Finally, we explain how the presence of an amount less than 0.1 at. % Cr in the 32 h milled Fe sample would not affect our previous conclusions. [S0163-1829(99)06021-X]

The as milled Fe powders, studied in our paper,¹ were analyzed through EDX (energy dispersive x-ray spectroscopy); for this, they were previously dispersed in ethanol by sonication and then dropped on a conventional carbon coated copper grid. In the hypothesis that impurities are introduced in the materials during the milling process, it is to be expected that the amount is larger in the powder milled for longer time. In Fig. 1, a typical EDX spectrum—obtained in a transmission electron microscope Philips CM200 FEG—relative to the 32 h milled Fe powder is shown. Only the peaks corresponding to Fe $K\alpha$ and Fe $K\beta$ are visible. Neither the presence of Cr nor of any other element has been detected, at least in an amount higher than 0.1 at. % which is the resolution limit of the EDX technique. We would like to remind that the peaks corresponding to Cr $K\alpha$ and Cr $K\beta$ should appear at 5.41 keV and 5.95 keV, respectively. In some areas of the sample, the EDX analysis has detected traces of oxygen: the presence of oxide is indicated in our manuscript and related to the small contribution observed at the low values of the hyperfine magnetic-field distributions (HFD).¹ As expected, the EDX spectra relative to the powders milled for shorter times (2, 4, 8, and 16 h) are absolutely similar to Fig. 1 and the only peaks which are visible are due to Fe. In light of these results, we can exclude the possibility that Cr impurities are present in the 32 h milled Fe powder in the amount deduced by Balogh *et al.* and reported in their Comment (0.3–0.5 at. %).

It was pointed out by the Comment’s authors that the application of steel milling tools introduces Cr impurities into the as-milled materials. However, by applying a careful control of the physical parameters governing the milling procedure and, specifically, the amount of transferred kinetic energy, it is possible to obtain a final product with an excellent degree of purity.^{2–4} For instance, if the milling process is carried out with a SPEX mill model 8000, it is recommendable, in order to obtain a good product, that the ball-to-powder weight ratio does not exceed 10:1. No impurities deriving from the milling tools have been detected by EDX

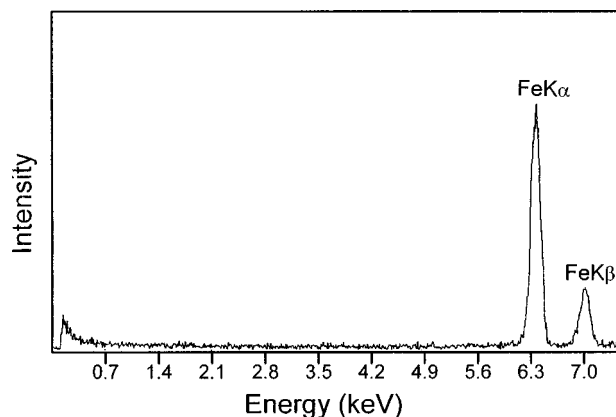


FIG. 1. EDX spectrum relative to the Fe powder milled for 32 h. See text for details.

analysis in Fe powders² or in Fe based alloys prepared in this way.³ On the contrary, the powders studied in Ref. 5, milled in a SPEX with a ball-to-powder weight ratio greater than 25:1, contained up to 5% of Cr. The only kind of impurity deriving from the milling process that is really not easy to avoid is Fe,^{3,6,7} and this is why iron powders can be considered as a model system for the study on mechanical attrition. It should also be pointed out that in the paper quoted as Ref. 2 in the Comment (and as Ref. 6 in this reply), dealing with fcc metals prepared by mechanical attrition, the only kind of contamination, detected by EDX, that has been mentioned is Fe. In this respect, it should be remarked that the milling technique used by Balogh *et al.* for preparing their samples, containing 2% Cr, is very different to that used in our case and therefore the final products should not be directly compared.

However, even considering that, in the Mössbauer spectrum relative to the as-prepared 32 h milled Fe, the contribution at 30 T in the HFD is *partially* due to Cr—note that just an amount of Cr less than 0.1 at. % must be reasonably thought to be present in the sample, against the 0.5 at. % that would be necessary to account for the whole contribution at 30 T—in our opinion this hypothesis does not affect the main conclusions of our research work.

The main experimental results, which constitute the fundamental content of the original paper,¹ are the two-component character of the Mössbauer spectra of the nanocrystalline Fe powders, the anomalous temperature dependence of the magnetization in as-milled powders and in samples annealed at 695 K and 770 K for 14 h, the appearance of the peak at 21 T in the HFD of the samples annealed at these temperatures, and the recovery of bulk Fe properties after thermal treatments at 970 K.

These results have been well accounted for considering the presence of a grain-boundary phase which rearranges and finally disappears, due to a concomitant grain growth process, upon annealing. Recently, it has been found^{8,9} that the phase resulting from the thermally induced grain boundaries rearrangement and giving rise to the peak at 21 T in the HFD, presents a structure consisting of magnetically ordered fcc Fe (lattice parameter of $3.51 \pm 0.05 \text{ \AA}$) with a magnetic order-disorder transition temperature of about 500 K; this

structure is rather stable and transforms into bcc Fe after 1 h thermal treatments in the region of 900 K. In fact, it should be pointed out that the prolonged annealing of 20 h at 970 K in Ar flux, described in our paper, was carried out just in order to reach the full certainty about the complete thermal stability of the sample. In that case the grain size grew up to more than 200 nm, but even a 1 h thermal treatment at 870–900 K, inducing a grain growth up to $\sim 80\text{--}90 \text{ nm}$,¹⁰ is sufficient to induce the disappearance of the HFD component in the Mössbauer spectrum.^{8,11}

As rightly remarked by Balogh *et al.*, the component at 30 T “is either not detectable or quite insignificant” in samples milled for times shorter than 32 h, but the above mentioned effects are already well visible in the powders milled for 8 h,^{1,8,11} even if some differences do exist as expected considering that different milling times imply different structural features of the various samples. This indicates that the incidental presence of 0.1 at. % Cr is substantially irrelevant to our conclusions. In particular, the strong increase in the HFD resonant area passing from 16 to 32 h milling—which for Balogh *et al.* constitutes an evidence of the presence of Cr impurities—has been well justified in the framework of the known model by Fecht *et al.*,¹² namely by invoking an increasing disorder of the grain boundaries with the milling time, in spite of an almost negligible grain size refinement.

Finally, we would like to stress that, in the hypothesis that 0.1 at. % Cr were present in the 32 h milled powder, one would obtain a possible explanation just for the presence and disappearance of a fraction of the contribution at 30 T in the HFD, whereas the HFD component (amounting to 17.4% of the total spectrum area) extends in the 20–35 T range and wholly disappears upon annealing.

In summary, Balogh *et al.* have carried out a study on the $\text{Fe}_{100-x}\text{Cr}_x$ ($x=2 \text{ at. \%}$, 5 at. \%) alloy and have used the results to demonstrate the effect of an apparent reduction in the Cr content after prolonged annealing at high temperature, as measured by Mössbauer spectroscopy. Since the EDX observations directly demonstrate the absence of Cr impurities in our samples, at least in amounts higher than 0.1 at. %, the arguments proposed by Balogh *et al.* are, in our opinion, insufficient to arouse any substantial doubt against our interpretation of the experimental results.

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