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Effect of the ball mass to sample mass relation in the magnetic and structural properties of $Fe_{0.6}Mn_{0.1}Al_{0.3}$ alloys prepared by mechanical alloying

J. F. VALDERRUTEN, G. A. PÉREZ ALCÁZAR*
Departamento de Física, Universidad del Valle, A.A 25360 Cali, Colombia
E-mail: geperez@univalle.edu.co
L. CIVALE
Centro Atómico de Bariloche and Instituto Balseiro, 8400 S.C., Bariloche, Argentina

$Fe_{0.6}Mn_{0.1}Al_{0.3}$ samples were prepared by mechanical alloying (MA) using the 6:1, 9:1 and 12:1 ratios between the ball mass and powder mass (BM/PM) and milling times of 3, 6, 9 and 12 h. Balls of 10 and 20 mm diameter were used. X-ray diffraction (XRD) studies showed that the 6:1 and 9:1 samples present, for all milling times and balls of 20 mm, the three elements, and in some cases (9:1 and 12:1 relations) the formation of a bcc disordered Fe-Mn-Al phase. The 12:1 samples with 12 h milling present only the bcc disordered phase. Mössbauer spectra (MS) of the 6:1 samples were fitted with a narrow hyperfine field distribution (HFD) with ≈32.6 T mean field (typical for pure Fe). The 9:1 spectra were fitted with a HFD and an increasing paramagnetic site which, according to X-ray results, correspond to impure Fe and the paramagnetic alloy, respectively. For the 12:1 samples, the spectra were fitted in a similar way but, for 12 h, the HFD is broad. In this case the alloy is totally consolidated and presents ferromagnetic and paramagnetic sites. When balls of 10 mm diameter were used the bcc formation is accelerated.

1. Introduction

Disordered Fe-Mn-Al alloys present an enormous scientific interest due the different magnetic phases detected such as paramagnetic (P), ferromagnetic (F), antiferromagnetic (AF), spin-glass (SG), reentrant spinglass (RSG) in the F and AF phases [1–3] and recently the pure and reentrant superparamagnetic (SP) phases [4]. Many reported works on this system concern on disordered alloys and only few are referred to samples prepared by MA. Giri *et al.* [5] showed that samples with 30 at.% Al and prepared by MA during 70 h present the RSG phase. Rico *et al.* [6] completed this study with samples milled during 12, 24, 48 and 72 h. Restrepo *et al.* [7] reported that MA $Fe_{0.6}Mn_{0.1}Al_{0.3}$ samples, with milling times of 24, 72 and 144 h, and a 12:1 BM/PM ratio, present a bcc disordered F phase with a soft magnetic character. The coercive forces decrease from 15 Oe for 144 h up to 10 Oe for 24 h (soft magnetic character). The magnetization at 8.5 kOe was near 70 emu./g for 24 h milling. In the present report we worked with the samples studied by Restrepo *et al.* [7], but prepared using lower milling times and BM/PM ratios and with two different ball diameters in order to study the steps formation of the bcc phase and the effect of the preparation parameters on the soft magnetic character of this ternary system.

2. Experimental method

MA $Fe_{0.6}Mn_{0.1}Al_{0.3}$ samples were prepared in a planetary ball mill with vials and balls of hardened chromium steel with 6:1, 9:1 and 12:1 BM/PM ratios and milling times of 3, 6, 9, and 12 h. Balls of 10 and 20 mm diameter (small and big balls) were used. X-ray patterns were taken using a Rigaku diffractometer with the Cu K_α radiation. MS were collected using a conventional spectrometer with a 57-Co(Rh) source and α-Fe as calibration sample. Cylindrical pressed powder samples of 3 mm diameter and 3 mm height were prepared for magnetization measurements using fields up to 5 T.

3. Results and discussion

3.1. X-ray studies

The microstructural changes as a result of MA can be followed by XRD method [8]. All the X-ray patterns of

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*Author to whom all correspondence should be addressed.

samples prepared by using big balls, the different times and 6:1 ratio (not showed) present the Fe, Mn and Al peaks, showing that under these milling conditions solid solution can not be produced. By using the same parameters but a 9:1 ratio, X-ray patterns of the prepared samples (not showed) present the Fe, Mn and Al peaks for all milling times. Besides, additional broad peaks of a bcc Fe-Mn-Al structure are observed for all the samples. This phase is the stable one for melted alloys with this composition [9]. Then the increase of balls number help the alloying process as a consequence of the increase of the mechanical energy given to the powders. However, this BM/PM ratio is not enough to the total consolidation the Fe-Mn-Al alloy inclusive for 12 h. Different results were obtained for samples prepared using big balls with 3, 6, 9 and 12 h and a 12:1 BM/PM ratio. When the $42 \leq 2\theta \leq 47$ range of the patterns are extended, as shown in Fig. 1a, decreasing peaks of Fe, Mn, Al can be identified, as well as an increasing broad one which is attributed to the bcc disordered Fe-Mn-Al alloy [6]. For milling time of 12 h, only the bcc peaks are detected and the phase is totally consolidated. Very similar results are obtained for samples prepared using small balls, a 6:1 BM/PM ratio and milling times of 3, 6, 9 and 12 h as can be seen in Fig. 1b. Then for small balls and low BM/PM ratio it is possible to produce the solid solution obtained for big balls and high BM/PM, showing that now the proccess is more efficient. This type of correlation between collision energy and ball size was also reported by Schaffer *et al.* [10]. When the BM/PM increases to 9:1 and 12:1, using small balls, the XRD results showed that above 6 h milling the bcc disordered solid solution is obtained.

The calculated lattice parameter, a, of the bcc phase for samples prepared with the 9:1 and 12:1 ratios and big balls remains practically independent of the alloying time with a value of $\approx 2.84 \pm 0.02$ Å, similar to that of α-Fe. The a value for samples prepared with these balls and 12:1 ratio increases between $\approx 2.84 \pm 0.01$ Å to $\approx 2.91 \pm 0.01$ Å, due to the increase of the Al content. Similar behaviors were reported for ordered and disordered melted Fe-Al alloys [11, 12] and Fe-Mn-Al alloys [7]. In this way for the 9:1 ratio the Al atoms do not diffuse inside the Fe lattice. The calculated a value vs. milling time, of the bcc solid solution, in samples prepared using small balls, is nearly constant for all the times with a value $\approx 2.91 \pm 0.01$ Å for the 9:1 and 12:1 samples. This confirm that under these conditions the bcc ternary alloy is consolidated and its Al content is the same for all the times. For samples with a 6:1 ratio, the a parameter increases with the milling time from 2.85 ± 0.03 Å up to 2.91 ± 0.01 Å according to the increase of the Al content of the alloy and its consolidation process.

Using the Scherrer formula [13] the mean crystallite sizes of the bcc phase were calculated. For samples produced with big balls and 9:1 and 12:1 BM/PM ratios, the bcc grain size is practically constant with a value of $\sim 80 \pm 10$ Å for all the milling times. For samples prepared using small balls and the different ratios, the

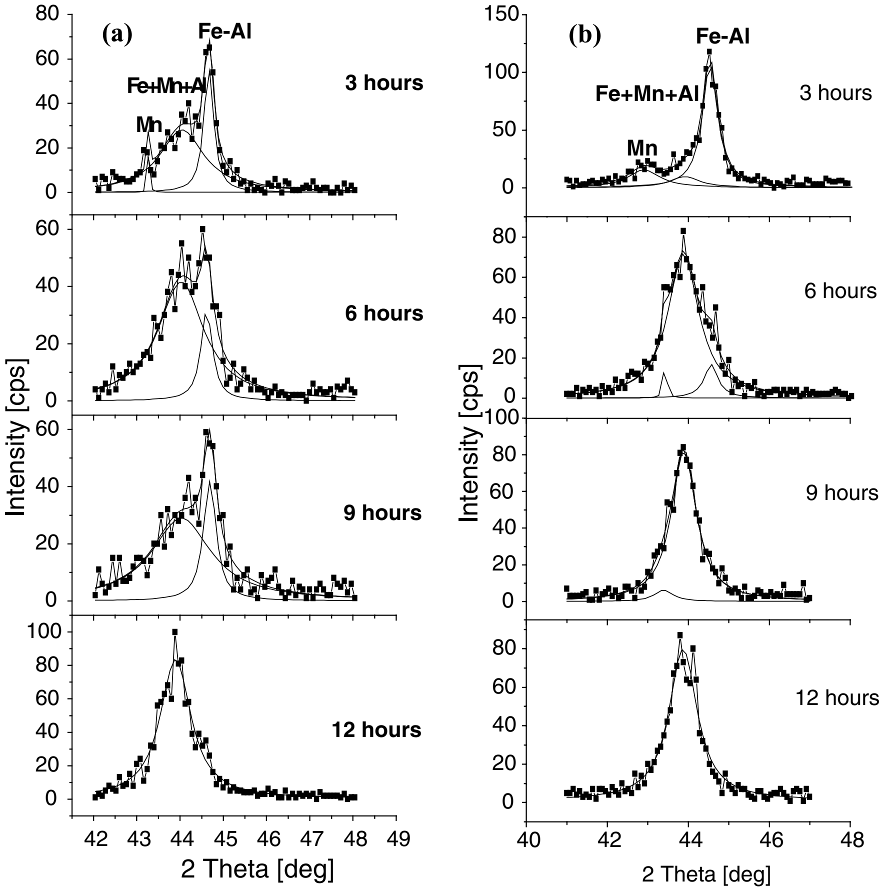


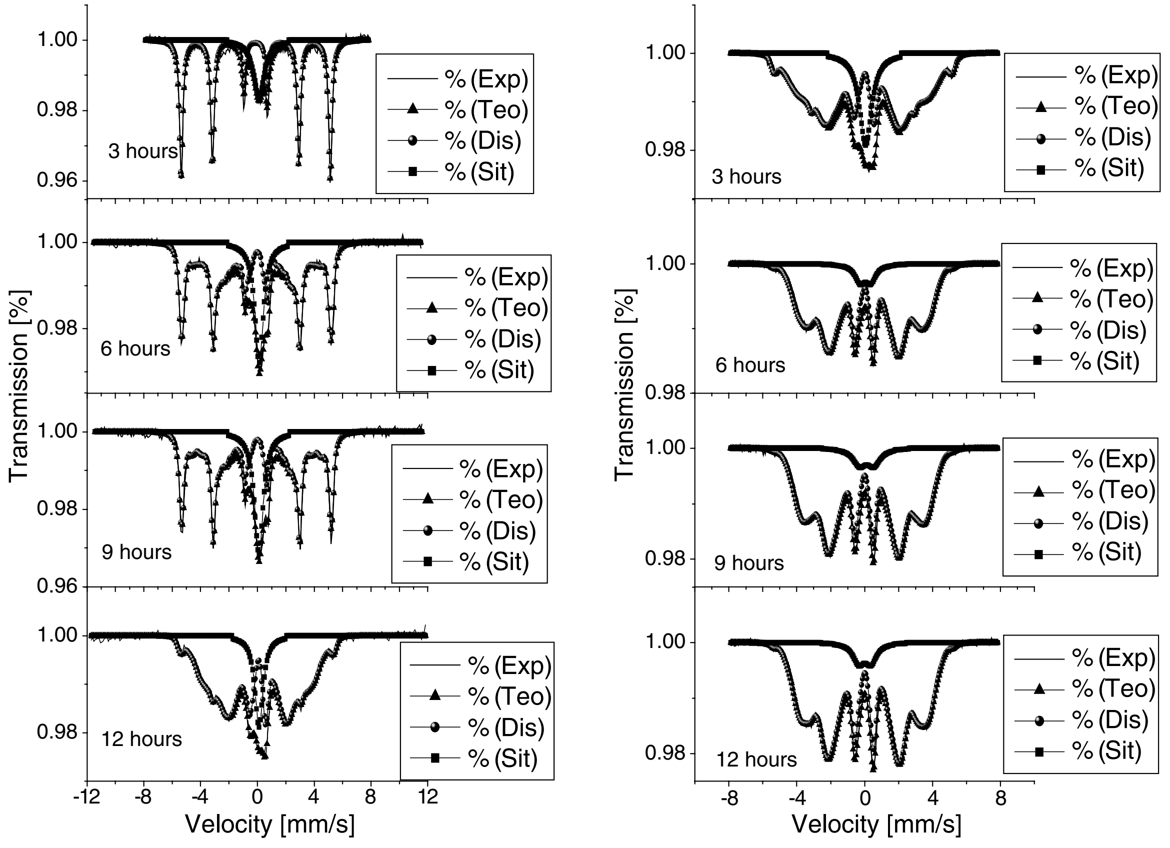
Figure 1 (a) Zoom of the principal peaks of the X-ray patterns, fitted with Lorentzians, of the samples prepared for different milling times, using balls of 20 mm and a 12:1 BM/PM ratio and (b) the same as (a) for samples milled at different times with balls of 10 mm and a BM/PM ratio of 6:1.

crystallite size presents a little increase from ∼ 100 Å for 3 h up to ∼140 ± 10 Å for 12 h. For the last conditions the mean grain size is larger than that obtained with big balls as previously reported [14]. Typical values of 80 Å is reached for most bcc metals [15]. The increase of the grain size is one of the steps of the MA process of fragile systems, which is characterized by a continuous increase of the grain size followed by their breaking, until the grain size is stabilized and the alloy is conformed.

3.2. Mössbauer studies

The MS at room temperature (RT) of the samples prepared by milling for all the times, a 6:1 ratio and big balls are similar to that of α-Fe, in accordance with the XRD results. The MS obtained for samples with a 9:1 ratio and big balls (not showed) present a sextet and an increasing broad paramagnetic line with the milling time. The narrow HFD used to fit the spectra has a mean field of 32.7 T nearly that of α-Fe. The increasing paramagnetic site, according to the XRD results, can be attributed to the ternary disordered Fe-Mn-Al alloy poor in Fe atoms.

Fig. 2a shows the MS at RT of samples prepared during 3, 6, 9 and 12 h, a ratio of 12:1 and big balls. The spectra were fitted with a HFD and a broad paramagnetic line. The progressive broadening of the HFD and the increase of the paramagnetic line can be noted. These facts are a consequence of the increase, in a random way, of the number of Al and Mn around the Fe atoms increasing the number of paramagnetic sites and decreasing the ferromagnetic sites. For the milling tome of 12 h, the bcc disordered alloy is totally consolidated (as showed by XRD), and its spectrum was fitted with a broad HFD and a paramagnetic site. The HFD corresponds to Fe sites rich in Fe atoms and the paramagnetic line to Fe sites rich in Al and Mn atoms. This fit shows the disordered character of the alloy. MS of samples prepared with a 6:1 ratio, milling times of 3, 6, 9 and 12 h and small balls, are very similar to those showed in Fig. 2a for samples prepared using a 12:1 ratio, the same milling times and big balls. Again it can be concluded that the small balls are more efficient to produce MA. Fig. 2b shows the MS obtained for samples prepared with a 12:1 ratio, milling times of 3, 6, 9 and 12 h and small balls. Their lines are broader than those obtained for the samples prepared using big balls. The spectrum of 3 h milled sample was fitted using a broad HFD and a broad singlet, whereas for big milling times the spectra were fitted with a broad HFD and a broad doublet. The XRD studies showed that these samples are totally consolidated in the bcc disordered phase. Then, in these samples the bcc phase present paramagnetic sites showing asymmetric charge distribution around the Fe atoms which correspond to Fe sites rich in Al and Mn atoms as nearest neighbors, and ferromagnetic sites with Fe atoms rich in Fe atoms as nearest neighbors. MS of samples prepared with a 9:1 ratio, milling times of 3, 6, 9 and 12 h and small balls, are practically the same as showed in Fig. 2b in accordance with the XRD



(a) **(b)**

Figure 2 Mössbauer spectra at RT for samples prepared with a 12:1 BM/PM ratio for: (a) different milling times and big balls and (b) small balls and different times.

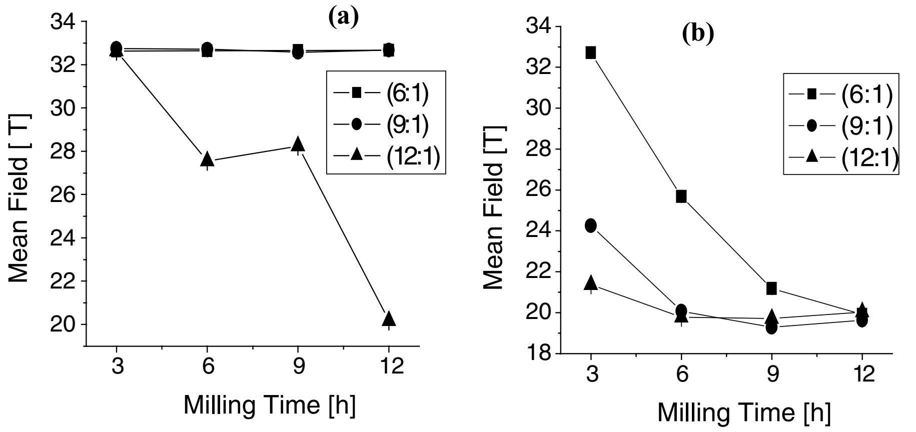


Figure 3 Mean field vs. milling time of samples prepared using: (a) big balls and (b) small balls.

results. The reported MS for melted $Fe_{0.6}Mn_{0.1}Al_{0.3}$ alloy [16] is similar to those showed in Fig. 2b for 6, 9 and 12 h and its X-ray pattern is also similar to those patterns obtained here and not showed. Then the milling of sample using small balls and relations and times bigger than 9:1 and 6 h, respectively, permit to reproduce the corresponding melted alloy. This behavior was also reported by Wolski *et al.* [17] for the Fe-Al system.

The evolution of the fitted mean hyperfine field (MHF) for different ratios and times using big balls is shown in Fig. 3a. For 6:1 and 9:1 ratios it can be noted that the MHF remains nearly constant for all times. In this case the Al and Mn atoms present low diffusion inside the Fe lattice without disturbing the local Fe field. For the 12:1 relation, the MHF decreases from $\approx 32.63 \pm 0.12$ up to $\approx 20.17 \pm 0.13$ T, showing the diffusion process of the Al and Mn atoms inside the Fe lattice to conform the ternary alloy. Fig. 3b shows the MHF curves for different ratios and times using small balls. It can be noted the continuous decreases for the 6:1 ratio and the constant value between 6 and 12 h for the 9:1 and 12:1 ratios. This confirms that in the first case the Al and Mn atoms are continuously diffusing in the Fe lattice reducing the mean field [18, 19], while for the second case the alloy is consolidated and its mean field remains constant. These conclusions are confirmed by the curves of the isomer shift (δ) vs. time for all the prepared samples (not showed). For 6:1 and 9:1 ratios and big balls, δ remains nearly constant (~ -0.12 mm/s), near the of α-Fe value. For 9:1 and 12:1 ratios and small balls, δ remain nearly constant (~ 0.05 mm/s), near that of melted bcc alloy, and for 12:1 and 6:1 samples produced with big and small balls, respectively, δ increase from that of pure Fe to that of melted bcc alloy as a consequence of the increase of the number of Al atoms which reduce the s electron density in the Fe nucleus in a similar way as reported previously [20].

In according with the MS results, which detect broad P sites, and the XRD results, which prove that the grains are of nanometric size, it is possible to postule the presence of SP clusters. MS at low temperatures with and without external magnetic field is now in progress in order to explore this possibility.

3.3. Magnetization studies

Finally, from the hysteresis loops of some samples it was possible to obtain the coercive force (H_c) and the magnetization at 5 T. At 5 T, all the samples showed magnetic saturation. Fig. 4 shows the curves (full lines) of the obtained H_c vs. milling time for samples with 12:1 (a) and 9:1 (b) ratios using big balls and small balls, respectively. It can be observed that the H_c values decrease with the milling time. For the 12:1 ratio

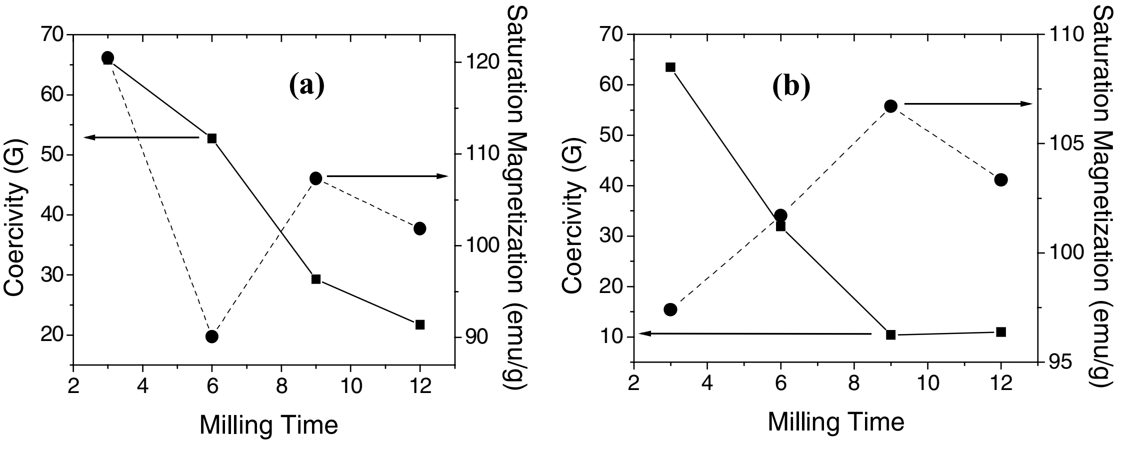


Figure 4 Coercive force (full line) and saturation magnetization (dashed line) vs. milling time for samples prepared using: (a) big balls and ratio 12:1 and (b) small balls and ratio 9:1.

and big balls, H_c decreases from 65 for 3 h up to 20 Oe for 12 h, while for the 9:1 ratio and small balls the values change from 63 for 3 h up to 8 Oe for 9 h. Restrepo *et al.* [7] found a value of 10 Oe for the sample prepared with the ratio 12:1, 24 h and big balls. Then using small balls and small BM/PM ratio only 9 h were necessary to obtain a similar H_c value. In Fig. 4, the saturation magnetization vs. milling time for samples prepared with big balls and the 12:1 ratio (a) and small balls and the 9:1 ratio (b) are showed (dashed lines). For 12:1 ratio and big balls, the magnetization values present a maxima of 120 emu/g for 3 h, when the majority phase is the Fe and another maxima of 107 emu/g. For 9 h and small balls the maxima value is 106 emu/g. The conclusion is that the use of small balls, a ratio of 9:1 and 9 h milling permit to improve the soft magnetic character of the samples reported by Restrepo *et al.* [7], i.e., decreases the H_c values from 10 to 8 Oe and increases the magnetization values from 70 to 106 emu/g.

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References

1. M. A. KOBEISSI, *J. Phys.: Condens. Matter.* **3** (1991) 4983.
2. H. BREMERS, CH. JARMS, J. HESSE, S. CHAJWASILIOU, K. G. EFTHIADIS and Y. TSONKALAS, *J. Magn. Magn. Mater.* **140** (1995) 63.
3. LIGIA E. ZAMORA, G. A. PÉREZ ALCÁ ZAR, A. BOHÓ RQUEZ, J. F. MARCO and J. M. GONZÁLEZ, *J. Appl. Phys.* **82** (1997) 6165.
4. LIGIA E. ZAMORA, G. A. PÉREZ ALCÁZAR, J. A. TABARES, A. BOHÓRQUEZ, J. F. MARCO and J. M. GONZÁLEZ, *J. Phys.: Condens. Matter.* **12** (2000) 611.
5. ANIT K. GIRI, LIGIA E. ZAMORA, G. A. PÉREZ ALCÁZAR and J. M. GONZÁLEZ, *IEEE Trans. Magn.* **31** (1995) 4023.
6. M. M. RICO, M. MEDINA and G. A. PÉREZ ALCÁZAR, *Hyperf. Inter.* **128** (2000) 503.
7. J. RESTREPO, G. A. PÉREZ ALCÁZAR and J. M. GONZÁLEZ, *ibid.* **122** (1999) 189.
8. E. HELLTEM, H. J. FECHT, Z. FU and W. L. JOHNSON, *J. Appl. Phys.* **65** (1989) 305.
9. D. J. CHAKRABARTI, *Met. Trans.* B. **8** (1977) 121.
10. G. B. SCHAFFER and P. G. McCORNICK, *ibid.* A **23A** (1992) 1285.
11. G. A. PÉREZ ALCÁZAR and E. GALVÁO DA SILVA, *J. Phys. F: Met. Phys.* **17** (1987) 2323.
12. G. P. HUFFMAN and R. M. FISHER, *J. Appl. Phys.* **38** (1967) 735.
13. B. D. CULLITY, "Elements of X-ray Diffraction" (Adisson-Wesley Pub. Co., 1967).
14. J. S. BENJAMIN, *Sci. Amer.* **5** (1976) 234.
15. C. C. KOCH, *Nanostruct. Mater.* **2** (1993) 109.
16. J. RESTREPO, G. A. PÉREZ ALCÁZAR and J. M. GONZÁLEZ, *J. Appl. Phys.* **87** (2000) 7425.
17. K. WOLSKI, G. LECAER, P. DELACROIX, R. FILLIT THÉVENOR and J. LE COZE, *Mater. Sci. Eng.* A. **97** (1996) 207.
18. A. ARROT and H. SATO, *Phys. Rev.* **114** (1959) 1420.
19. M. B. STERNS, *ibid.* **147** (1966) 439.
20. R. RODRÍGUEZ and G. A. PÉREZ ALCÁZAR, *Phys. Stat. Sol.* B. **220** (2000) 441.

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