

POINT DEFECTS AND THE B2 TO FCC TRANSFORMATION IN MILLED FeRh

LUKE S.-J. PENG and GARY S. COLLINS *

Department of Physics, Washington State University, Pullman, WA 99164, * collins@wsu.edu

ABSTRACT

Mössbauer measurements were made on FeRh containing 52 atomic percent (at.%) Fe after mechanical milling for different times in a high-energy SPEX 8000 vibrator mill. Hyperfine fields are compared with fields for annealed ferromagnetic (F) samples having the B2 structure in the range 52-58 at.% Fe. For annealed F samples, hyperfine field shifts of -1.66 T and -1.12 T were detected at majority Fe_{Fe} and minority Fe_{Rh} probes due to Fe_{Rh} antisite atoms in, respectively, the first and second atomic shells. Analysis of dipolar fields indicates that the magnetization lies along the $\langle 110 \rangle$ direction. The transformation from F B2 phase to a metastable paramagnetic fcc phase was observed that was half complete in 8 minutes. Analysis of spectra for the milled F B2 phase show that a second point defect was produced by milling that induces shifts of $+6$ T and $+8.5$ T, respectively, at majority and minority probes. Many-spectra fits were made under different defect models that led to the conclusion that milling produces point defects in the triple-defect configuration: 2 Fe-vacancies and 1 Fe-antisite atom. Defect concentrations were determined and show that the fractional concentration of vacancies on the Fe-sublattice increases linearly with milling time, reaching 3 at.% after 8 minutes, a very large value. The rate of transformation from B2 to fcc phase appears to be independent of the concentrations of point defects in the B2 phase, indicating that the transformation is purely stress-induced, as in a martensite transformation.

INTRODUCTION

Severe plastic deformation associated with high-energy mechanical milling frequently leads to formation of non-equilibrium, metastable phases. One way in which non-equilibrium phases can be stabilized is by adding enough point defects to the parent, equilibrium phase so that its free energy exceeds the energy of a related, metastable phase. For highly ordered intermetallic compounds, the formation energy of point defects is often relatively low while their migration energy is high, so that it is possible to store an appreciable amount of energy in the form of point defects such as vacancies and antisite atoms. In previous work on milled intermetallics having the B2 (CsCl) structure, we used hyperfine probe techniques to detect point defects with atomic-scale resolution and to measure their concentrations. For PdIn, [1] vacancy concentrations on the two sublattices were measured using the method of perturbed angular correlation of gamma rays with $^{111}\text{In}/\text{Cd}$ probes and found to increase to several percents after only a few minutes of milling and to saturate thereafter. For FeAl, [2] concentrations of vacancy and antisite defects were determined from ^{57}Fe Mössbauer measurements and, unlike for PdIn, milling reduced the vacancy concentration and increased the numbers of antisite-atoms.

Between 35 and 50 at.% Fe, FeRh solidifies in a disordered fcc phase, has a first-order transition to an ordered B2 phase at about 1600 K, and becomes magnetically ordered below about 700 K.[3] Magnetic ordering was first elucidated by neutron scattering and Mössbauer measurements.[4] Magnetic B2 FeRh has been known to undergo a transition to the nonmagnetic, metastable fcc phase by stress or plastic deformation [5] In the present work, we determine the types and concentrations of point defects in the B2 phase during plastic deformation by mechanical milling using Mössbauer measurements on ^{57}Fe probes. Our goal is

to determine whether or not there is a correlation between defect concentrations in the B2 phase and the transition to a nonequilibrium phase. Detection of point defects was not possible in the earlier Mössbauer measurements on FeRh [4] because linewidths were very broad. Resolution is much better than in our earlier work on FeAl [2] because the defects can be resolved here by magnetic hyperfine field shifts that they induce.

EXPERIMENT

Samples of FeRh having 52,54,56 and 58 at.% Fe were made by melting high-purity foils together (>3N5) under argon in a small arc-furnace and splat-quenching in order to make foil samples appropriate for Mössbauer absorbers. Samples were given a crystallizing anneal at 1000 C for 1 hour and cooled in furnace prior to measurement. Measurements reported here were made in triangular, constant-acceleration mode at 293(2) K using a Ranger MS-1200 spectrometer, with spectra measured at positive and negative accelerations folded together. A gamma-ray source of ^{57}Co in Rh purchased from Amersham International was used that yielded a very narrow linewidth when extrapolated to zero absorber-thickness, only 0.21(1) mm/sec. Milling was carried out under argon in a tungsten carbide vial using a SPEX 8000 vibrator mill. Two WC ball bearings were used and the ball to sample mass ratio was always greater than 20, making for very high-energy impacts. FeRh is exceedingly hard and, unlike for FeAl or PdIn, the milled material never fragmented into a powder even after milling for 15 minutes. Milled foil fragments were withdrawn from the milling vial after milling for time intervals up to 15 minutes and assembled into a mosaic absorber for Mössbauer and x-ray measurements. X-ray measurements made using a Siemens 5000 diffractometer showed that annealed samples were entirely B2 phase and milled samples contained B2 and fcc phases, with the fcc phase increasing with milling time. The mean B2 crystallite size determined by x-rays was 8 nm after 15 minutes of milling. A search for $L1_0$ distortions of the fcc phase showed broadening of the $\langle 200 \rangle$ reflection consistent with a range of c/a distortions of the fcc structure between 1.00 and 1.01.

ANALYSIS AND RESULTS

Annealed samples. Fig. 1 shows Mössbauer spectra for annealed samples having 52-58 at.% Fe. All spectra are fitted well assuming only the presence of ferromagnetic B2 FeRh. Spectra consist of a superposition of magnetic sextets, each attributed to a discrete configuration of probe atoms and defects in the first two atomic shells. In the perfect B2 structure, Fe atoms are surrounded by 8 Rh atoms in the first near-neighbor (nn) shell and 6 Fe atoms in the second shell. For Fe-rich samples, excess Fe atoms go onto the Rh sublattice where they are surrounded by 8 Fe atoms in the first shell and 6 Rh atoms in the second shell. The large-area sextet with outer-line splitting of 8.8 mm/sec and the small-area sextet with splitting of 12.5 mm/sec correspond to majority Fe_{Fe} and minority Fe_{Rh} probes without defects in their first two shells. The Fe_{Rh} probe has a larger splitting (and hyperfine field) because it is surrounded by 8 Fe atoms, as in pure iron metal. In general, a Fe_{Fe} probe will have Fe_{Rh} antisite defects in its first shell and no defects in its second shell whereas a minority Fe_{Rh} probe will have no defects in its first shell and Fe_{Rh} defects in its second shell.

Milled samples. Fig. 2 shows selected Mössbauer spectra for milled samples. The most obvious difference to spectra for annealed samples is the appearance and growth of a large paramagnetic line near zero velocity that has previously been attributed to the metastable fcc phase. In addition, new sextets were fitted that were not observed in annealed FeRh and which are attributed to deformation-induced defects other than Fe_{Rh} .

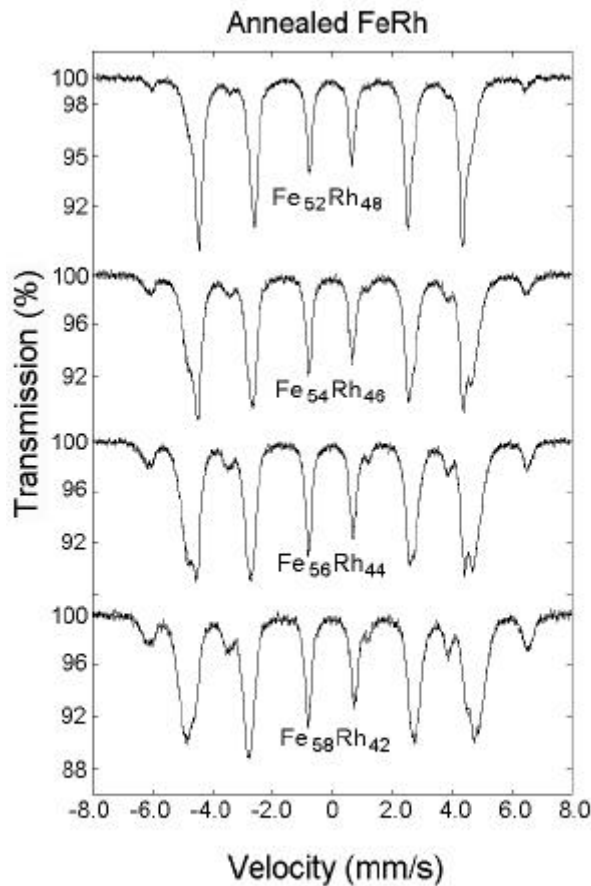


Fig. 1. Mössbauer spectra of annealed B2 FeRh. Magnetic sextets are visible for majority Fe_{Fe} probes (splitting 8.8 mm/s), minority Fe_{Rh} probes (splitting 12.5 mm/s) and satellite sextets due to Fe_{Rh} antisite defects in the first two atomic shells around the probes.

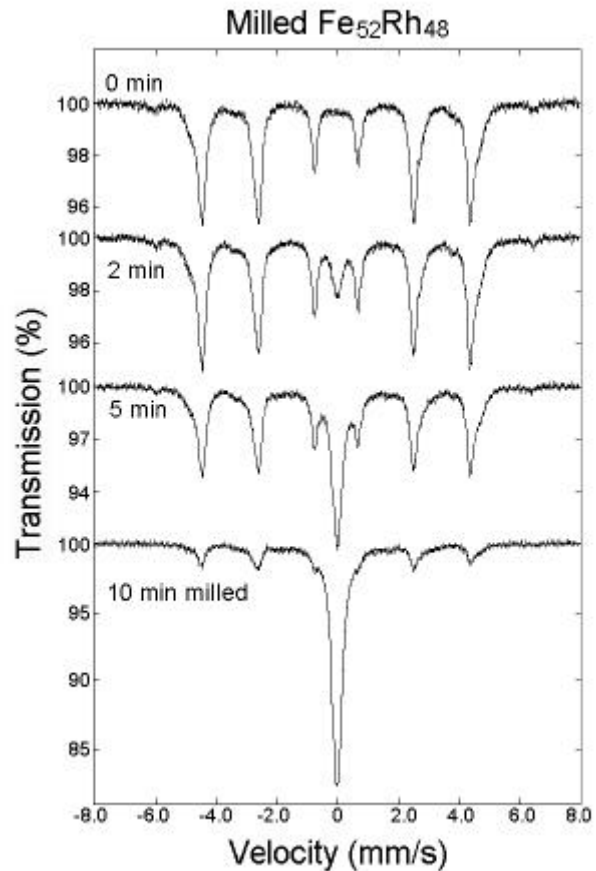


Fig. 2. Mössbauer spectra of milled FeRh. The magnetic B2 phase is progressively replaced by a nonmagnetic, metastable fcc phase. In addition, the milled magnetic phase exhibits new sextets attributed to vacancies on the Fe sublattice.

Defect combinations produced by milling. Point defects are produced as a consequence of deformation processes such as nonconservative motion of jogged dislocations. Ignoring interstitial defects because of their very high energy, the possible elementary defects are vacancies, V_{Fe} or V_{Rh} , and antisite atoms, Fe_{Rh} or Rh_{Fe} , on the two sublattices. Elementary defects must be produced in definite combinations that preserve locally the overall ratio of Fe and Rh atoms. Possible combinations considered in the present study include the antisite-atom pair (Fe_{Rh} and Rh_{Fe}), Schottky vacancy pair (V_{Fe} and V_{Rh}), and triple defect ($2V_{Fe}$ and Fe_{Rh}). The triple defect can be thought of as forming from a Schottky pair by transfer of an Fe_{Fe} atom into an adjacent V_{Rh} . A major finding of the present work is that the dominant deformation-induced defect combination is the triple defect.

Local environment method for fitting spectra. Spectra were fitted to a superposition of signals from ^{57}Fe probe atoms in the different local atomic environments, as in our previous work on FeAl. [2] The signals include a paramagnetic singlet for the fcc phase and magnetically split sextets for the B2 phase for probe atoms on Fe or Rh sublattices having defects in the nearest two atomic shells. The following assumptions were used in fitting the B2 phase signal:

1) The B2 phase is homogeneous. 2) Elementary point defects are randomly located. 3) Sextet intensities (areas) for having a specified number of defects in the first two shells are proportional to the binomial probabilities. 4) Hyperfine interactions (monopole, magnetic dipole and electric quadrupole) depend only on defects in the nearest two atomic shells of the probes. 5) Defects produce isotropic monopole and magnetic hyperfine disturbances that depend only on the defect type and distance from the probe. 6) When more than one defect is simultaneously present, monopole and hyperfine magnetic field shifts are linearly additive. 7) Small fitted quadrupole interactions were taken to be a perturbation of the much larger magnetic splittings. 8) Recoilless fractions are equal for all probes on one sublattice, although they might differ between sublattices. 9) Lines are adequately approximated using the Lorentzian lineshape, with line broadening due to resonant self-absorption accounted for by a uniform, broadened linewidth. 10) Inhomogeneous broadening due to defects more distant than the second shell can be adequately described by line-broadening that is proportional to magnetic splitting. It can be seen that the quality of the fits shown in Figs. 1 and 2 is excellent.

Dipole fields due to moment disturbances of defects. Although the magnetization in ferromagnetic FeRh has been reported to be along $\langle 100 \rangle$, [6,4] spectra for B2-phase FeRh could only be fitted well assuming that the magnetization M is not along $\langle 100 \rangle$, but along $\langle 110 \rangle$. When M is along $\langle 100 \rangle$, as in Fe metal, the component of the dipole field from a near-neighbor moment disturbance along the direction of the hyperfine field (or M), proportional to $(3\cos^2\theta - 1)$, in which θ is the angle between M and the direction to the defect, is zero. However, this is not the case in general. Much better fits were obtained assuming that M lies along or very near $\langle 110 \rangle$, for which there is a dipole splitting into two components of equal amplitude. The $\langle 111 \rangle$ direction could be definitely excluded. The fitted dipole splitting was $\pm 0.57(3)$ T, too large to be caused solely by a defect moment at the nn distance, and probably explained by disturbances of moments of ^{57}Fe probes adjacent to Fe_{Rh} defects.

Fe antisite atoms in annealed FeRh. Spectra were fitted assuming that only Fe_{Rh} defects reflecting deviations from stoichiometry were present. Fitted parameters included the fractional concentration of Fe_{Rh} defects and hyperfine field shifts at Fe_{Fe} probes in the first neighbor shell and at Fe_{Rh} probes in the second shell. [7] For an alloy of nominal composition $\text{Fe}_{1+s}\text{Rh}_{1-s}$ the fractional concentration s of Fe atoms on the Rh sublattice is s . Fitted values of s were in excellent agreement with nominal compositions determined from the masses of elements melted together. Fitted values of the hyperfine field shifts ΔH due to Fe_{Rh} defects are listed in Table 1 together with other relevant hyperfine parameters. Parameters were found to be somewhat dependent on the composition, and only values for 52 at.% Fe ($s = +0.04$) are listed here. Also listed for the first shell Fe_{Rh} defect is the dipole splitting ΔH_{dip} and the ratio of the intensity of

Table I. Hyperfine fields and defect-induced shifts in B2 and fcc FeRh (52 at.% Fe)

Probe	H / T ^a	IS(mm/s) ^b	Defect	Shell	$\Delta H/H$	$\Delta H / T$	$\Delta H_{\text{dip}}/T$	$f_{\text{dip}}(\%)$
Fe_{Fe}	-27.28(1)	+0.029	Fe_{Rh}	1	+0.061(1)	-1.66(3)	0.57(3)	56(2)%
			V_{Fe}	2	-0.31(1)	+8.5(3)	-	-
Fe_{Rh}	-38.64(5)	+0.265	V_{Fe}	1	-0.15(6)	+5.8(2.3)	-	-
			Fe_{Rh}	2	+0.029(2)	-1.12(8)	-	-
fcc	0	+0.063	-	-	-	-	-	-

a. Hyperfine field at ^{57}Fe probes having no defects in the first two atomic shells. Field is assumed negative (i.e., directed opposite to the magnetization).

b. Isomer shift measured with respect to alpha-Fe.

one dipole component to the intensity of both components. The value 56% is very close to the value 50% expected for M along $\langle 110 \rangle$ and inconsistent with the value 75% that would be expected if M were along $\langle 111 \rangle$.

Triple defects in milled B2 FeRh. Two additional hyperfine field shifts were detected in preliminary fits of the spectra for milled samples. These are attributed to the production of one or more additional elementary point defects by milling. That the additional shifts were not caused by sample contamination during milling was confirmed by the observation that the additional shifts in a sample milled for 15 minutes completely disappeared upon annealing. The type of disorder produced by milling was assumed to be either dominantly antistructure, Schottky, or triple-defect type, as defined above. Spectra were fitted to obtain s , marking the deviation from stoichiometry, and the fractional concentration of the selected defect combination. Poor fits were obtained when it was assumed that milling produced antistructure atom pairs and, in addition, the fitted stoichiometry parameter s decreased essentially to zero for long milling time, an unphysical result. Attempts to fit the spectra assuming that Schottky vacancy pairs were produced were likewise unsuccessful, but can not be excluded with as much certainty at the antistructure defect model because the greater numbers of elementary defects (3) and field shifts (6). The best fits were obtained assuming that triple-defects are produced. Fitted values of s and of the fractional concentrations of Fe_{Rh} and V_{Fe} defects are shown as a function of milling time in Fig. 3. As can be seen, s remains constant in the course of milling, and the vacancy concentration increases monotonically with milling time, reaching 3.5% after 10 minutes. A comparable vacancy concentration was found during milling of PdIn. [1]

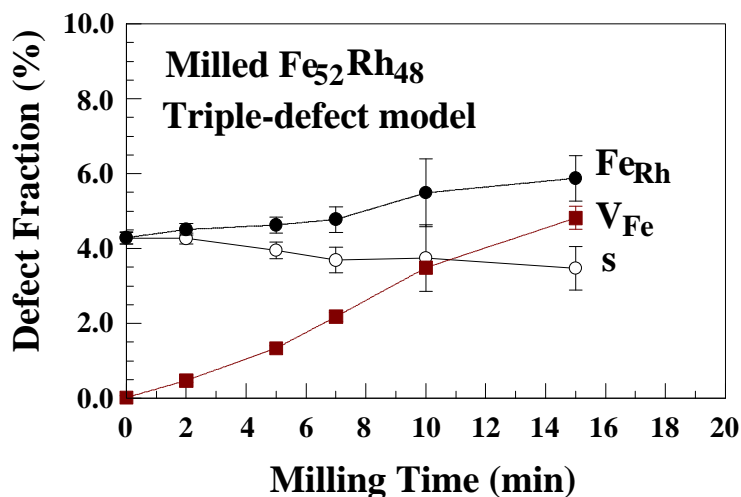


Fig. 3. Fitted stoichiometry parameter s and fractional concentrations of Fe_{Rh} and V_{Fe} defects for B2 FeRh having 52 at.% Fe ($s^{\text{@}} + 0.04$), from fits of spectra measured after milling for the indicated times.

Independent support for our finding that triple defects are produced by milling of B2 FeRh comes from the x-ray measurements of the lattice parameter a , which was 0.299077(2) nm for the annealed 52 at.% sample. The variation of a with milling time is assumed to reflect the point defects produced during milling, and was -0.000076 nm/min. The negative value is consistent with the general rule of thumb for intermetallics that vacancies shrink the lattice parameter whereas antisite atom pairs expand the lattice. The effect of Fe_{Rh} defects by themselves was determined from the variation of a with composition in annealed samples: from 52 to 58 at.% Fe a changed by -0.000205 nm per at.%Fe. From these values and trends in Fig. 3, it can be shown that the shrinking effect of V_{Fe} is two times greater than of Fe_{Rh} .

Time evolution of the B2 to fcc transformation. If the transformation were triggered or accelerated by the presence of point defects, or their associated stored energy, then one might expect to observe an "incubation time" during which defect concentrations build up prior to the start of transformation. Mass fractions of the B2 and fcc phases are equal to the fitted area fractions in the approximation that recoilless fractions of the two phases are the same. In Fig. 4, the fitted area fractions are shown versus milling time. Transformation is observed to start immediately after milling begins, so that it does not appear necessary to develop a defect concentration before transformation is initiated. A rough plot made from Fig. 4 of the fractional transformation of the B2 phase per minute exhibits an increase during milling, but this trend could have been caused by periodic extraction of material to make samples during milling since the ball-to-sample mass ratio gradually increased, leading to higher-energy milling.

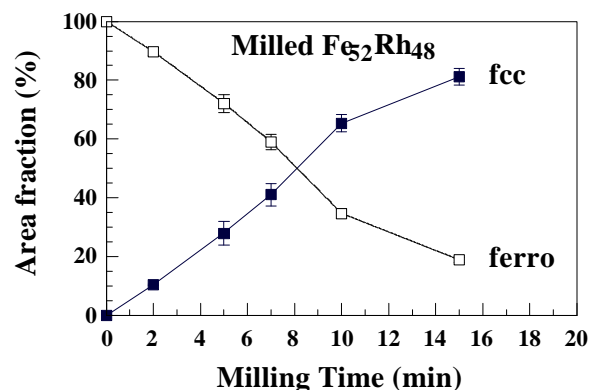


Fig. 4. Area fractions of fcc and ferromagnetic B2 Mössbauer spectral components versus milling time. There is no evidence of an incubation time before the onset of the transformation from the B2 phase to the metastable fcc phase

CONCLUSION

The possibility of a correlation between production of point defects and the transformation to a metastable phase during mechanical milling was examined. No such correlation was clearly evident, suggesting that the B2-to-fcc transformation in milled FeRh is a diffusion-less stress-induced transition akin to a martensitic transition except that in FeRh both phases are cubic.

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