Phonon density of states of γ-Fe precipitates in Cu

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The phonon density of states of γ-Fe precipitates in a Cu matrix were studied as a function of particle size by using nuclear resonant inelastic scattering of synchrotron radiation. The host metal affects the phonon density of states of the precipitates up to 30 nm in diameter. Larger precipitates are free from the influence of the host metal and show rather similar phonon density of states to those of fcc-Fe alloy bulk specimens such as stainless steel (310ss) and $Fe_{70}Ni_{30}$ at room temperature although γ-Fe is unstable at room temperature under an atmospheric condition. Careful observation, however, yields characteristics of γ-Fe precipitates in the phonon density of states.

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I. INTRODUCTION

The recent development of a synchrotron radiation x-ray source made it possible to study phonon density of states of a specimen with resonant nuclei using a nuclear resonant inelastic scattering method (NRISM).[1] In order to study phonon, the NRISM has an advantage over the neutron inelastic scattering method in some cases. Since information only from the resonant nuclei is obtainable in NRISM, it is possible to study partial phonon density of states of a constitutional atom (resonant atom) in an alloy. Furthermore, far smaller size specimen is enough to study phonon states comparing with neutron inelastic scattering method. The most tractable resonant nucleus would be ^{57}Fe and several phonon data studied by NRISM for the specimens with ^{57}Fe nuclei have been reported until now.[2–5] The present paper treats phonons of fcc-Fe (γ-Fe) precipitates in a Cu matrix. fcc-Fe is stable only in the temperature range between 1185 and 1667 K under normal atmospheric conditions. However, Fe precipitates grown in a supersaturated Cu-Fe alloy after an appropriate thermal treatment retain the γ phase even at room temperature. The precipitates are known to be spherical in shape. Their sizes depend on the duration and temperature of the precipitation anneal. Thus, the particle sizes are easily controlled by the thermal treatments. The nuclear resonant inelastic scattering method seems to be the most suitable way to study the phonon states of this system. Since the phonon states of only the resonant nuclei are observable in the NRISM, we can obtain the information on the phonons of the γ-Fe precipitates solely apart from the Cu matrix. This is impossible for neutron inelastic scattering method. Since γ-Fe precipitates are coherent with the lattice of the Cu matrix and have a little smaller lattice spacing than the Cu matrix, the γ-Fe precipitates with small particle sizes would be exposed to strong expansive force through the interface. Then, we can study how the host metal affects and how far the effect extends to the phonon states of the precipitates. Recently, nanoparticle precipitates have received great attention due to many technological applications such as improved mechanical properties. Thus, knowledge on the phonons in precipitates would give us a great contribution to the development of new materials.

In the present paper, we report the phonon density of states for the γ-Fe precipitates with various particle sizes in the Cu matrix studied at room temperature by using NRISM and discuss the effect of host metals and the difference from the bulk γ-Fe specimens.

II. SAMPLE PREPARATION AND EXPERIMENTS

Several ingots of supersaturated CuFe solid solutions with 3 at. % of ^{57}Fe were prepared in a furnace with a carbon electrode in Ar gas atmosphere. All ingots were homogenized by annealing at 1323 K for 24 h and quenched into water. Then, precipitation anneal was performed at 848 K for various aging periods for the most of specimens. Precipitation particle sizes were estimated using the empirical equation derived by Borrelly *et al.*[6] For the largest precipitates ($d \sim 80$ nm), the annealing temperature was 998 K. Coherent precipitates with Cu matrix are known to be stable up to 130 nm in diameter.[7] Thus, carefully prepared specimens are considered to include no bcc Fe precipitates at least for the particle sizes of the present experiments. Prior to the measurements, sample surfaces were mechanically polished with fine-mesh emery papers and deeply etched in dilute ($\sim$10%) nitric acid.

The nuclear resonant inelastic scattering experiments were performed at the beam line BL09XU of SPring-8. A double-crystal Si(111) premonochromator was used to handle the high heat load of undulator radiation and the radiation was monochromatized to the bandwidth of 3.2 meV (FWHM) with a nested high-resolution monochromator consisting of asymmetric Si(511) and asymmetric Si(975) channel-cut crystals. The incident beam energy was varied

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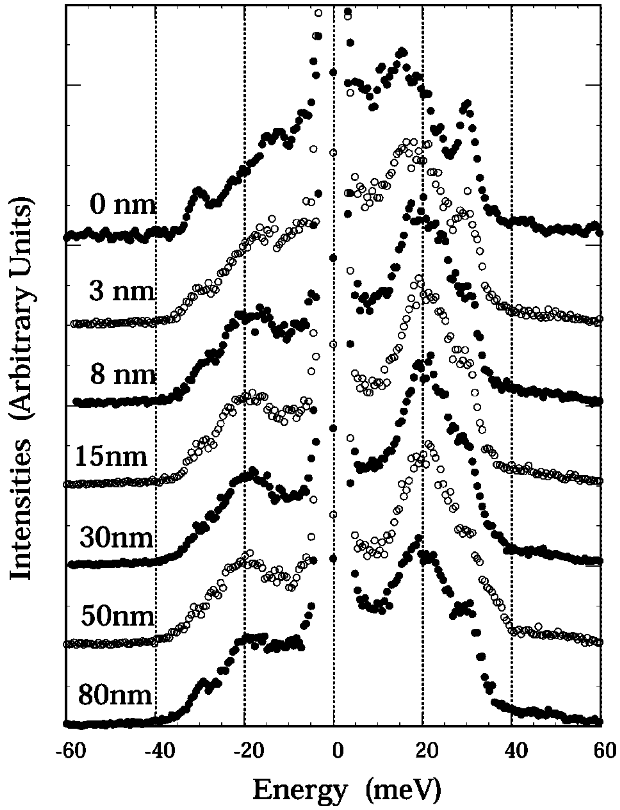

FIG. 1. Nuclear resonant inelastic scattering spectra at room temperature for γ-Fe precipitates with various particle sizes. Here, minus energy indicates the x-ray energy gain process. The data for 0 nm diameter indicate those for the isolated Fe impurities in Cu published by Seto *et al.* (Ref. 5).

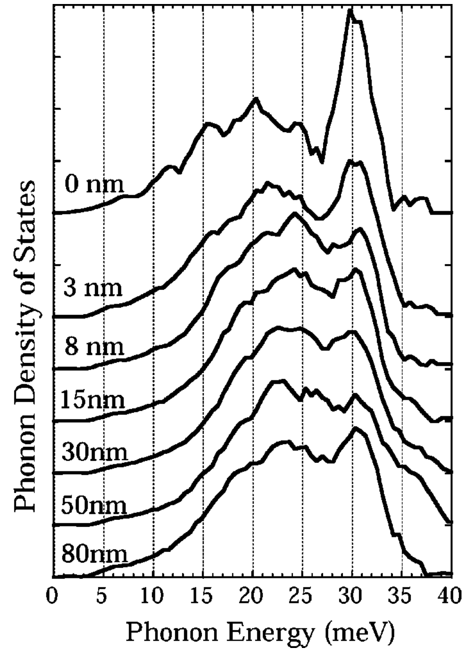

FIG. 2. Experimental phonon density of states for various sizes of γ-Fe precipitates in Cu. The 0 nm data are again those for the isolated Fe impurities in Cu for comparison.

around the first nuclear resonant energy of ^{57}Fe (14.413 keV). The incident beam intensity was monitored with an ionization chamber and a beam flux monitor. A Si-avalanche photodiode (APD) detector with an active area of 25 mm^2 was used to observe the delayed photons in the nuclear resonant scattering from ^{57}Fe precipitates in the Cu matrix.

III. EXPERIMENTAL DATA AND DISCUSSION

We first discuss the size effect of the γ-Fe precipitates in the Cu matrix. After discussing the effect of the Cu matrix to the precipitates, phonon DOS of the matrix free γ-Fe precipitates is compared with those for bulk specimens of γ-Fe, γ-Fe alloys, and bcc-Fe.

A. The effect of the matrix to the small particles

The precipitation particle sizes with diameters of 3, 8, 15, 30, 50, and 80 nm were studied at room temperature. Nuclear resonant inelastic scattering spectra for these specimens are given in Fig. 1. The extreme limit of the smallest precipitates would be an isolated Fe impurity in Cu. Phonon DOS of the isolated ^{57}Fe impurity in Cu was previously studied by Seto *et al.* using Cu-0.1 at. % ^{57}Fe alloy.[5] The experimental data for the isolated ^{57}Fe atoms in Cu are also shown in Fig. 1 as a zero nm diameter specimen for comparison. The spectra for the small precipitates are obviously different from those for the large precipitates, verifying that phonons of the small precipitates are under the influence of the host metal. The differences are distinct for the sharp peak around 30 meV and the position of the low-energy peak. The spectrum for the smallest precipitates ($d=3$ nm) is the closest to that of the isolated ^{57}Fe and changes of the spectra seem to be continuous as the particle size increases.

After the correction of multiphonon process and deconvolution of the data with the instrumental resolution function,[8] we obtain experimental phonon density of states (DOS) for the specimens with various sizes of γ-Fe precipitates. Results are shown in Fig. 2. In the case of isolated Fe impurity in Cu, vibration of Fe atom would be essentially the same as that of the host matrix except for the differences of atomic mass and force constant between the impurity and the host. Seto *et al.* compared the phonon DOS of Fe impurity in Cu and that of pure Cu.[5] Rather high density peak was observed above the cut off frequency of Cu phonons and they explained it using broadened localized phonon mode due to the mass and force constant differences between the host and impurities. For the smallest precipitates ($d\sim3$ nm), phonon DOS is similar to that of the isolated Fe in Cu, but appreciable change is observed in the low-energy peak which mainly reflects around the zone boundary phonons of the transverse mode. The same trend is observed with increasing the precipitation particle sizes up to 15 nm in diameter, but no appreciable change is found above 30 nm precipitates, indicating that the influence of the host matrix would be negligible for these precipitates. On the other hand, high-energy peak intensity decreases with increasing the particle sizes but the peak position is not sensitive to the precipitation particle sizes. Strong intensity at high-energy peak for the isolated Fe reflects that the majority of Fe atoms contributes to the localized phonon. Thus, part of the high-energy peak for 3 nm

TABLE I. Fractions of atomic pairs as a function of particle size.

Fe Particle Size(nm)	Cu-Fe(%)	Fe-Fe(%)
Isolated	100	0
3	32	68
8	13	87
15	7	93
30	4	96
50	2	98
80	1	99

precipitates may come from the localized phonon modes due to the isolated Fe atoms dissolved in the host metal at the aging process although the solubility of Fe in Cu at 848 K is less than 0.1 at. %.

It should be noted that the atomic mass (^{57}Fe) is the same for all the precipitates with various particle sizes in the present specimens. Thus, these changes of the phonon DOS should be ascribed to the interatomic forces. In the present case, two kinds of interatomic forces $f_{\text{Cu-Fe}}$ and $f_{\text{Fe-Fe}}$ must be considered. However, the effect coming from the direct coupling between Fe and Cu atoms $f_{\text{Cu-Fe}}$ would not be so strong. In Table I, atomic fractions located at the interface to the total number of Fe atoms are listed for various precipitate sizes. If the force constant $f_{\text{Cu-Fe}}$ contributes predominantly, the effect should disappear for the precipitates with 15 nm diameter because the surface fraction is already less than 10%. Furthermore, if this is the case, observed data should be composed of two spectra, the one for the interface atoms and the other for the inner atoms of the precipitates. Obtained phonon spectra, however, show continuous change up to 30 nm precipitates, indicating that the influence of the host metal is not confined to the interface area but extends through out the particles uniformly and the effect is gradually weakened with increasing the particle sizes. Insensitivity of the high-energy peak position to the particle size supports this argument because it suggests that the atomic force constant between Cu and Fe is almost the same as that between Fe atoms. Thus, the effect should be ascribed to the interatomic forces between Fe atoms $f_{\text{Fe-Fe}}$. One possible explanation would be an interatomic distance between Fe atoms. As mentioned above, γ-Fe precipitates are coherent with the Cu matrix and the lattice spacing of γ-Fe is slightly smaller than that of Cu (difference is about 0.7%). The γ-Fe precipitates are exposed to a strong expansive force and small precipitates actually have larger lattice spacings than the large precipitates as shown in x-ray diffraction data.[7] Thus, the interatomic forces $f_{\text{Fe-Fe}}$ for small precipitates would be weaker than those for large precipitates. Recently, Fultz *et al.* studied the phonon DOS for bcc ^{57}Fe nanocrystalline with the size of about 10 nm using NRISM. They reported that the low-energy phonon below 15 meV shows an enhancement of the DOS curve although its origin is not fully understood.[4] The similar enhancement of the DOS curve for the low-energy region is also reported by Frase *et al.* for nanocrystalline of milled Ni_3Fe by using neutron inelastic scattering.[9] These phenomena may look similar to the common feature with that observed for small γ-Fe precipitates, but it should be noted that circumstances for these nanocrystallines and γ-Fe precipitates in Cu are completely different. Particle size dependence of the phenomenon for bcc-Fe and Ni_3Fe nanocrystallines has not been reported yet, but it would give us some information on this problem. In Table II, recoilless fractions, averaged force constants and mean frequencies calculated from these spectra are listed as a function of precipitate size. The table supports that the influence of the host metal extends the particles up to 30 nm in diameter.

The γ-Fe precipitates with diameters larger than 30 nm are considered to be free from the influence of the Cu host. It is interesting that the magnetism (spin density wave state) in cubic γ-Fe precipitates also shows the size dependence for the particles smaller than 30 nm in diameter.[10] However, various properties of the structural phase transition (transition temperature, amplitude, and wavelength of the atomic displacement wave) observed for γ-Fe precipitates in Cu at low temperature depend on the particle size even beyond 80 nm in diameter.[11] The present data confirm that the microscopic (electronic) properties such as phonons and magnetism of the precipitates with a diameter larger than 30 nm are already free from the influence of the host metal, but the structural phase transition, which includes the volume expansion and external shape change, is still under the influence of the host metal even for far larger precipitates.

B. Phonon DOS of γ-Fe

As discussed above, the precipitates larger than 30 nm in diameter are free from the influence of the host metal. Then, the phonon DOS for the γ-Fe precipitates larger than 30 nm is considered to be the same as that of bulk fcc-Fe. However, remember that an fcc phase of Fe is unstable at room temperature under the atmospheric condition. Thus, to study the

TABLE II. Recoilless fraction, averaged force constant and mean frequency calculated from the experimental phonon spectra.

Particle size (nm)	3	8	15	30	50	80
Recoilless fraction	0.719 (0.044)	0.746 (0.006)	0.754 (0.006)	0.757 (0.006)	0.768 (0.004)	0.734 (0.004)
Averaged force const (N/m)	132 (9)	134 (10)	138 (8)	139 (8)	147 (9)	139 (10)
Mean frequency (meV)	23.48 (0.03)	23.79 (0.04)	24.16 (0.03)	24.33 (0.03)	25.00 (0.03)	24.12 (0.03)

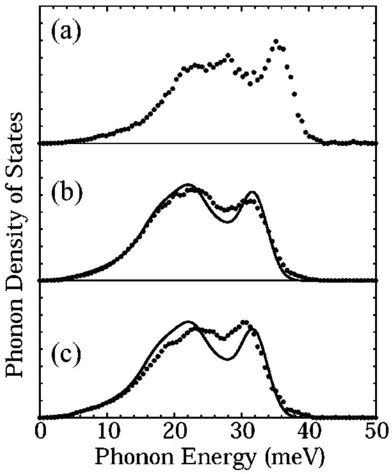

FIG. 3. Experimental phonon density of states at room temperature for (a) bcc-Fe foil, (b) stainless steel (310ss), (c) γ-Fe precipitates in Cu ($d = 80$ nm). Solid lines in (b) and (c) indicate the calculated phonon density of states for $Fe_{70}Ni_{30}$ using the dispersion relation curves determined by neutron inelastic scattering.

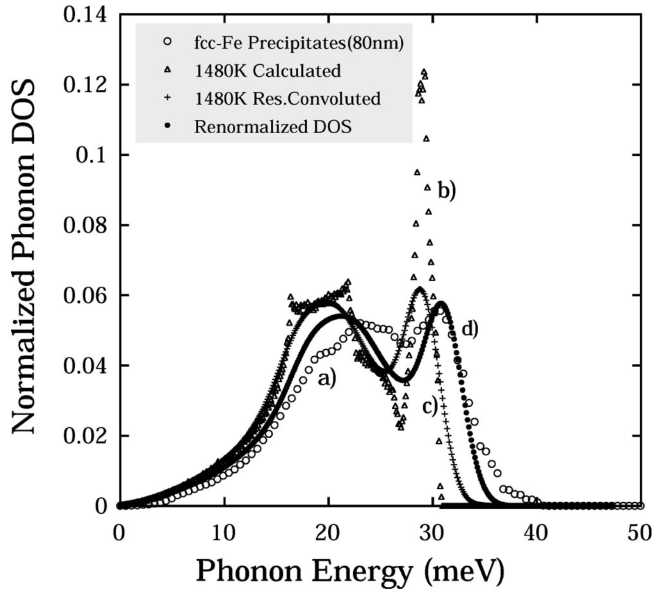

FIG. 4. Comparison with the stable γ-Fe bulk specimen. (a) (Open circles) Experimental phonon DOS for γ-Fe precipitates ($d = 80$ nm). (b) (Open triangles) Calculated phonon DOS for bulk γ-Fe using the atomic force constants determined by neutron inelastic scattering at 1480 K. (c) (Crosses) Resolution convoluted phonon DOS at 1480 K. (d) (Closed circles) Renormalized phonon DOS for the γ-Fe bulk specimen. Normalization factor was determined so as to fit to the high-energy peak position.

phonon state of γ-Fe at unstable temperature and to compare it with those of fcc Fe alloys and stable γ-Fe at high temperature are very interesting problem. In order to compare the results, stainless steel (310ss) and bcc-Fe foil were also studied using NRISM under the same experimental conditions as for the γ-Fe precipitates in Cu. Experimental phonon DOS curves derived from the nuclear resonant inelastic scattering spectra for γ-Fe precipitates with 80 nm in diameter, stainless steel and bcc-Fe foil are given in Fig. 3. In this figure, calculated phonon DOS for the $Fe_{70}Ni_{30}$ alloy is also shown by solid line. In this calculation, atomic force constants derived from phonon dispersion relations determined by neutron inelastic scattering were used.[12] To compare the experimental data, the Gaussian resolution function for the present measurement with a 3.2 meV FWHM was convoluted to the calculated phonon DOS in this figure. Difference between bcc-Fe and fcc-Fe is obvious from this figure. The shape of the phonon DOS for γ-Fe precipitates is almost similar to that of the stainless steel and the calculated phonon DOS for the $Fe_{70}Ni_{30}$ alloy. However, careful observation gives us a characteristic of γ-Fe precipitates. The low-energy peak in the phonon DOS for γ-Fe precipitates is located at slightly higher energy side than those for the stainless steel and $Fe_{70}Ni_{30}$ although the mass of Fe^{57} is heavier than those of the stainless steel and $Fe_{70}Ni_{30}$ (the averaged mass of $Fe_{70}Ni_{30}$ is 56.71). Lattice spacings at room temperature for both systems are almost equal [$a(\gamma\text{-Fe}) = 3.589$ Å and $a(Fe_{70}Ni_{30}) = 3.586$ Å]. Thus, the present results indicate that the inter-atomic forces for the shear mode of γ-Fe precipitates are stronger than those for the fcc-Fe alloys.

The pure γ-Fe bulk specimen is available at high temperature. The phonon dispersion relation curve for the γ-Fe bulk specimen was determined by using neutron inelastic scattering at a stable temperature (1428 K).[13] We calculated the phonon DOS for bulk specimen using the reported atomic force constants by the same procedure as that adopted for the $Fe_{70}Ni_{30}$ alloy. The results were compared in Fig. 4. Since the measuring temperature is different, direct comparison has no meaning. In order to compare the experimental data with this calculation, the renormalized DOS which was multiplied by a factor 1.07 to the calculated phonon energies is also given in this figure. The renormalization factor was determined to fit the high-energy peak position of the DOS curve. Again the low-energy peak in the phonon DOS curve for the γ-Fe precipitates is located at higher-energy side than that for the bulk specimen. It is unknown at the present stage whether the characteristic of the phonon DOS for γ-Fe precipitates is caused by the instability of the fcc-Fe at room temperature.

It is rather surprised that the phonon DOS of γ-Fe precipitates shows broadly the same shape as that of stable fcc-Fe alloys in spite that fcc-Fe is unstable in the normal atmospheric conditions at room temperature. The data suggest that the metastable γ-Fe phase has similar atomic potential to that of stable fcc bulk Fe. The instability of γ-Fe precipitates would be reflected to an unharmonic component of phonons which is not discussed in the present paper. Temperature variation of phonon DOS in γ-Fe precipitates in Cu may give us information on the unharmonic effect because γ-Fe precipitates undergo the structural phase transition at low temperature.[11]

IV. CONCLUSIONS

Phonon DOS of γ-Fe precipitates in Cu was studied using NRISM. In this method, since the information only from the resonant nuclei is obtainable, we can measure the phonons of the precipitates solely. For small precipitates ($d<30$ nm), influence of the host metal is appreciable. The effect of the host metal is not confined to the interface between the host metal and precipitates, but rather seems to extend to whole precipitates uniformly. For large precipitates, influence of the host metal is negligible and the precipitates show the phonon DOS of original γ-Fe.

The shape of phonon DOS of γ-Fe precipitates is almost similar to those for fcc-Fe alloys ($Fe_{70}Ni_{30}$ and stainless steel). The low-energy phonons, however, have lower density of states than these fcc-Fe alloys, suggesting that the dispersion relation curves for the transverse phonon modes have steeper slopes although atomic masses and lattice spacings are nearly equal for these systems. These points are very interesting if we remember that γ-Fe is unstable at room temperature under atmospheric conditions. Temperature variation of phonon DOS for γ-Fe precipitates includes very interesting problems because γ-Fe precipitates undergo a structural phase transition at low temperature at which drastic phonon softening is reported by the sound velocity measurements.[14] Temperature variation measurements of phonon DOS for γ-Fe precipitates are now in progress.

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