Anisotropic phonon density of states
in FePt nanoparticles with $L1_0$ structure

Ferromagnetic FePt with an $L1_0$ structure is composed of alternating stacked layers of Fe and Pt atoms along the c-axis (AuCu-type structure with $P4/mmm$ space group), as shown in Fig. 1(a). The structure gives rise to a marked crystal anisotropy, which is responsible for the uniaxial magnetic easy axis along the c-axis (i.e., perpendicular to the Fe and Pt layers). Since the uniaxial magnetic anisotropy energy (K_u) of approximately 6×10^6 J/m^3 is extremely large, the superparamagnetic limit at room temperature can decrease to approximately 3 nm in particle size [1,2].

It is interesting to determine whether the phonon states of $L1_0$-FePt also have an anisotropy as large as its magnetic energy. We investigated the phonon states of $L1_0$-FePt utilizing ^{57}Fe nuclear resonant inelastic scattering with synchrotron radiation [3]. By developing the chemical method named the "SiO$_2$-nanoreactor method" [4], we prepared $L1_0$-FePt nanoparticles that have a well-ordered $L1_0$ single-crystalline structure with a single magnetic domain. $L1_0$-FePt nanoparticles synthesized by this method can be made dispersible in various solvents, and the orientation of the easy axis (i.e., c-axis) of the dispersed nanoparticles can be controlled by applying an external magnetic field [5]. By taking these advantages of the method, we prepared $L1_0$-FePt nanoparticle/polystyrene composites, in which c-axis aligned nanoparticles are well dispersed and tightly fixed. These composites are suitable for observing an anisotropic phonon state along different directions of the lattice using ^{57}Fe nuclear resonant inelastic

scattering with synchrotron radiation. Indeed, we observed the anisotropic partial density of states (PDOS) in $L1_0$-FePt and compared it with the PDOS calculated in the bulk state by the first-principles method.

The average particle diameter of the prepared $L1_0$-FePt nanoparticles and its standard deviation were 5.1 and 1.2 nm, respectively. To prepare an $L1_0$-FePt nanoparticles/polystyrene composite, $L1_0$-FePt nanoparticles (3.2 wt.%) were dispersed in a styrene monomer solution with azobisisobutyronitrile (1.0 wt.%), which acts as an initiator of the radical polymerization of styrene. The solution was then kept at 60°C for 18 h in argon atmosphere while applying an external magnetic field of 9 T. During this process, the free radical polymerization of styrene proceeds almost completely and the thus-formed polystyrene matrix acts as a binder to fix $L1_0$-FePt nanoparticles with the c-axis aligned parallel to the external magnetic field. A photograph of the obtained $L1_0$-FePt nanoparticles/polystyrene composite is shown in Fig. 1(b). The cylindrical composite is 10 mm in diameter and 12 mm in height. The direction of the aligned c-axis of the $L1_0$-FePt nanoparticles was perpendicular to the top and bottom faces of the composite. Figure 1(c) shows the schematic illustration of a cross-sectional view of the composite. The orientation of the c-axis of the nanoparticles in the composite has a finite distribution because the fixation process using an external field was affected by the thermal effect [6].

The phonon states of the c-axis aligned $L1_0$-FePt nanoparticles were investigated by ^{57}Fe nuclear resonant inelastic scattering at beamline **BL09XU**. The storage ring was operated in the 11-bunch train mode. An SR of 14.41 keV with a bandwidth of 2.5 meV excited ^{57}Fe nuclei in the sample. By detuning the energy of the SR within approximately 100 meV at approximately the ^{57}Fe nuclear resonant energy, we can obtain the probability of the creation and annihilation of phonons at the energies. Four avalanche photodiode detectors were use to collect the intensity scattered into a large solid angle. The energy spectra of the composite were measured under the conditions in which the direction of incident X-rays was set parallel or perpendicular to the direction of the aligned c-axis of the $L1_0$-FePt nanoparticles. We call these the parallel and perpendicular geometries, respectively.

The energy spectra measured for the composite at 300 and 10 K in the parallel geometry are shown in Figs. 2(a) and 2(b), respectively. The spectra
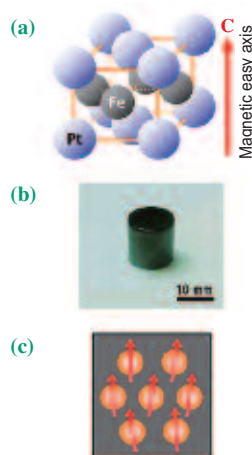

Fig. 1. **(a)** Schematic illustration of the $L1_0$ structure of FePt. **(b)** Photograph of the $L1_0$-FePt nanoparticles/polystyrene composite. **(c)** Schematic illustration of the cross-sectional view of the composite.

measured under the perpendicular geometry are shown in Figs. 2(c) and 2(d). The intense central peaks are due to the zero-phonon scattering by ^{57}Fe Mössbauer resonance. The side parts of the spectra show the probability of inelastic excitation with the creation (right-hand side) or annihilation (left-hand side) of phonons in the $L1_0$-FePt nanoparticles. The intensities of the spectra in the side parts show the PDOS at the energies in the lattice. The contribution of the zero-phonon Mössbauer resonance effect was subtracted and the multiphonon contributions were also subtracted using an iterative procedure [7]. The thus-obtained PDOS, which were determined from the phonon energy spectra measured at 10 K in the parallel and perpendicular geometries, are shown in Figs. 3(a) and 3(b), respectively. It is clearly shown that the PDOS observed in the parallel and perpendicular geometries are significantly different from each other. In Fig. 3(a), the spectrum consists of a strong peak at about 28 meV, which can be observed in the original experimental spectra of Figs. 2(a) and 2(b). In Fig. 3(b), the PDOS from the a-axis in the $L1_0$-FePt lattice has a distribution from 17 to 32 meV. These measurements also imply that the Debye temperature of $L1_0$-FePt along the c-axis is higher than that along the a-axis. This can be ascribed to the chain structure with alternating Fe and Pt atoms, which have very different masses, located only along the c-axis. To study the results from a theoretical point of view, we

calculated the PDOS of the $L1_0$-FePt in the bulk state by the first-principles method [8]. Figures 3(c) and 3(d) show the results of the calculation along the c- and a-axes, respectively. The calculated PDOS along the c-axis shown in Fig. 3(c) consists of a strong peak at about 28 meV, which is consistent with the experimental result. The calculated PDOS along the a-axis shown in Fig. 3(d) consists of two strong peaks at 18 and 24 meV. The results were in good agreement with the experimental results.

Fig. 3. Phonon densities of states (PDOSs) determined from the phonon energy spectra measured at 10 K in the (a) parallel and (b) perpendicular geometries. PDOSs calculated in the bulk state by the first-principles method for the (c) parallel and (d) perpendicular geometries.

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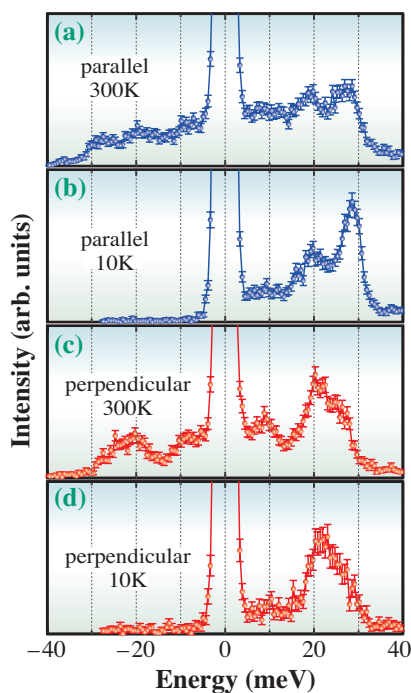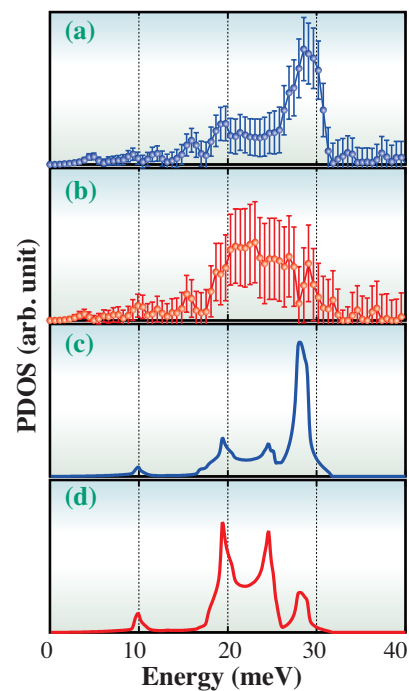
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Fig. 2. Phonon energy spectra of the composite measured at (a) 300 and (b) 10 K in the parallel geometry. Corresponding spectra measured at (c) 300 and (d) 10 K in the perpendicular geometry.

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