

Title	Anisotropic phonon density of states in FePt nanoparticles with L1 ₀ structure
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Anisotropic phonon density of states in FePt nanoparticles with $L1_0$ structureYoshinori Tamada,^{1,*} Ryo Masuda,^{2,3} Atsushi Togo,⁴ Shinpei Yamamoto,⁵ Yoshitaka Yoda,^{6,3} Isao Tanaka,^{4,7} Makoto Seto,^{8,3} Saburo Nasu,¹ and Teruo Ono¹¹*Institute for Chemical Research, Kyoto University, Uji 611-0011, Japan*²*Japan Atomic Energy Agency, Kouto 679-5148, Japan*³*CREST, Japan Science and Technology Agency, Kawaguchi 332-0012, Japan*⁴*Department of Materials Science and Engineering, Kyoto University, Kyoto 606-8501, Japan*⁵*Institute for Integrated Cell-Material Sciences, Kyoto University, Kyoto 606-8501, Japan*⁶*Japan Synchrotron Radiation Research Institute, Kouto 679-5198, Japan*⁷*Nanostructure Research Laboratory, Japan Fine Ceramics Center, Nagoya 456-858, Japan*⁸*Research Reactor Institute, Kyoto University, Osaka 590-0494, Japan*

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The phonon states of iron atoms in the easy-axis aligned $L1_0$ -FePt nanoparticles were investigated using ^{57}Fe nuclear-resonant inelastic scattering. It was revealed that the phonon density of states (PDOS) in the $L1_0$ -FePt has a pronounced anisotropy. To study the results from a theoretical point of view, we calculated the PDOS of the $L1_0$ -FePt in the bulk state by means of the first-principles method. The results were in good agreement with the experimental results.

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Ferromagnetic FePt with the $L1_0$ structure is composed of alternately 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 generates notable 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 $6 \times 10^6 \text{ J/m}^3$) is extremely large,¹ the superparamagnetic limit at the room temperature can decrease down to approximately 3 nm in particle size.² Therefore, the $L1_0$ -FePt nanoparticles are expected as one of promising candidates for the magnetic recording media in the near future.³⁻⁵ Recently, we have succeeded in preparing the $L1_0$ -FePt nanoparticles by developing the chemical method named “ SiO_2 -nanoreactor method.”⁶ Our previous studies revealed that the FePt nanoparticle synthesized by this method has well-ordered $L1_0$ single-crystalline structure with the single magnetic domain⁷ while the other chemical methods can prepare only FePt nanoparticle with disordered face-centered-cubic or partially ordered $L1_0$ structure.^{8,9} It is also worth noting that the $L1_0$ -FePt nanoparticles synthesized by this method can be made dispersible in various solvents and that the orientation of easy axis (i.e., c axis) of the dispersed nanoparticles can be controlled by an external magnetic field.^{10,11} By taking these advantages of the method, we also succeeded in preparing $L1_0$ -FePt nanoparticles/polystyrene composites, where the c -axis aligned nanoparticles are well dispersed and tightly fixed.¹² Our previous studies revealed that the c axis of the $L1_0$ -FePt nanoparticles in the composite had a preferred orientation with a finite distribution.¹²

These works have been performed with focusing on the application of the $L1_0$ -FePt nanoparticles for the magnetic recording media. However, the developed $L1_0$ -FePt nanoparticles/polystyrene composite is also suitable for observation of anisotropic phonon states along different directions of the lattice. The nuclear-resonant inelastic scattering of synchrotron radiation (SR) is a suitable method for investigation of anisotropic lattice dynamics.¹³ In fact, the first

observation of phonon states along several lattice directions was reported by Chumakov *et al.*,¹⁴ who revealed that the phonon density of states (PDOS) in FeBO_3 single crystal has notable anisotropy by using ^{57}Fe nuclear-resonant inelastic

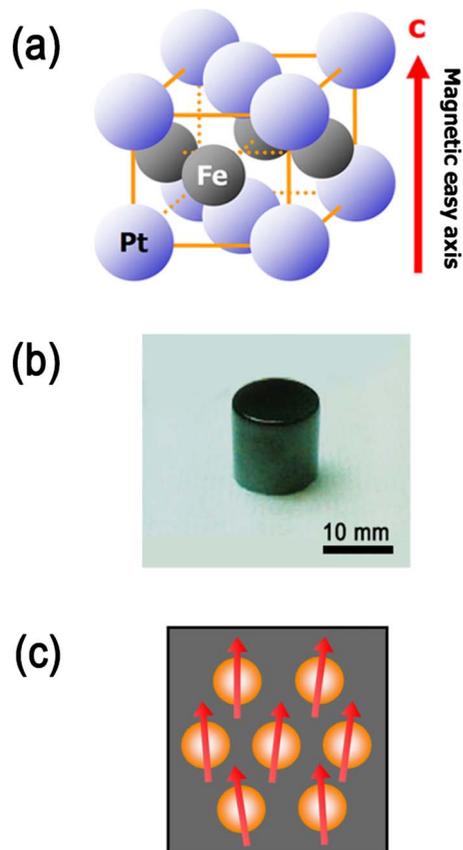


FIG. 1. (Color online) (a) Schematic illustration of the $L1_0$ structure of the FePt. (b) Photograph of the $L1_0$ -FePt nanoparticles/polystyrene composite. (c) Schematic illustration of the cross-sectional view of the composite.

scattering of SR. We can expect that clearer anisotropy of phonon states can be detected by measuring our sample. This is because we first obtained the single crystals of FePt with well-ordered $L1_0$ structure and the polystyrene matrix containing the assembly of the nanoparticles with the c axis aligned to certain direction. The polystyrene matrix is expected to be rather transparent to the hard SR x rays since it is composed of relatively light-weight elements (carbon and hydrogen). It is interesting to search whether the phonon states of $L1_0$ -FePt also has large anisotropy like its magnetic energy. Unfortunately, to our knowledge, there have been no reports concerning the phonon states in $L1_0$ -FePt single crystal so far. In this Brief Report, we investigated the phonon states of $L1_0$ -FePt nanoparticles by utilizing the ^{57}Fe nuclear-resonant inelastic scattering of SR. It was revealed that the lattice dynamics of the $L1_0$ -FePt has an anisotropic property, which is stronger than that of FeBO_3 . The anisotropic PDOS in the $L1_0$ -FePt were also calculated by a first-principles method.

The $L1_0$ -FePt nanoparticles were prepared by the SiO_2 -nanoreactor method.^{4,6} The synthesized nanoparticles had the uniform dispersibility with single-crystalline structure as the transmission electron microscopy indicated. The particle diameter was estimated to be 5.1 ± 1.2 nm. The $L1_0$ -FePt nanoparticles/polystyrene composite was prepared as follows; First, the $L1_0$ -FePt nanoparticles were dispersed in styrene monomer solution. Then, the solution was heated at 60°C for 18 h under argon atmosphere while applying an external magnetic field of 9 T. During this period, the free radical polymerization of styrene proceeded almost completely and thus-formed polystyrene matrix acted as a binder to fix the $L1_0$ -FePt nanoparticle with the c axis aligned parallel to the external field. We note that the transverse axes to c axis had nonorientated states in a plane perpendicular to the aligning direction. The movements and rotations of the nanoparticles were suppressed by the glassy polystyrene matrix at room temperature. The photograph of the obtained $L1_0$ -FePt nanoparticles/polystyrene composite is shown in Fig. 1(b). The cylindrical composite has the size of 10 mm in diameter and 12 mm in height. The direction of aligned c axis of the $L1_0$ -FePt nanoparticles is perpendicular to the top and bottom faces of the composite. Figure 1(c) shows the schematic illustration of cross-sectional view of the composite. We note that the orientation of c axis of the $L1_0$ -FePt nanoparticles in the composite has a finite distribution because the fixation process using the external field was affected by the thermal effect.¹²

The phonon states of the c -axis aligned $L1_0$ -FePt nanoparticles were investigated using ^{57}Fe nuclear-resonant inelastic scattering of SR at BL09XU in SPring-8. The storage ring was in the several electron-bunch modes with 29 electron-bunch trains in the period of 165.2 ns. The σ -polarized incident SR x rays with the bandwidth of 2.5 meV around the 14.413 keV ^{57}Fe nuclear resonance were produced using the high-heat load Si (111) monochromator and the high-resolution monochromator consisting of asymmetric Si (511) and Si (975) channel-cut crystals. By varying the energy of the SR within approximately 100 meV around the ^{57}Fe nuclear-resonant energy, we can obtain the probability of the creating and annihilating of phonons at the energies. Four-

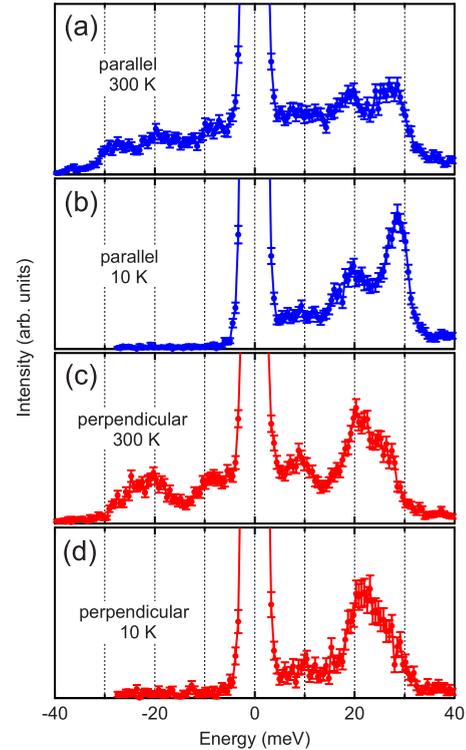


FIG. 2. (Color online) Phonon energy spectra of the composite measured at (a) 300 K and (b) 10 K under the parallel geometry. Corresponding spectra measured at (c) 300 K and (d) 10 K under the perpendicular geometry. The horizontal axis is an energy scale of incident x rays.

element avalanche photodiode detectors were employed for collecting the intensity scattered into a large solid angle. The energy spectra of the composite were measured under the conditions that the direction of incident x rays were set parallel or perpendicular to the direction of aligned c axis of the $L1_0$ -FePt nanoparticles. From now on, we call them parallel and perpendicular geometries, respectively.

The energy spectra measured with the composite at 300 and 10 K under the parallel geometry are shown in Figs. 2(a) and 2(b), respectively. The corresponding spectra measured under the perpendicular geometry are also shown in Figs. 2(c) and 2(d). The intense central peaks in all spectra come from elastic scattering by ^{57}Fe Mössbauer effect. The side parts of the spectra show the probability of inelastic excitation with creations (right-hand side) or annihilations (left-hand side) of the phonon in the $L1_0$ -FePt nanoparticles. In other words, the intensities of the spectra in the side parts show the density of phonon modes at the energies in the lattice. Although the spectra basically have a symmetric shape, the relative intensities between the right and left side depend on the measurement temperature. Since the annihilations of phonon rarely happen at low temperature, the intensity of left-hand part in the spectra measured at 10 K [Figs. 2(b) and 2(d)] is significantly suppressed in comparison with that measured at 300 K [Figs. 2(a) and 2(c)]. The both energy spectra measured at 300 and 10 K show significant difference between the parallel and perpendicular geometries. In case of the parallel geometry, the spectrum consists of two

peaks at approximately ± 19 and ± 28 meV. On the other hand, in case of the perpendicular geometry, the spectra basically consist of one broad peak at approximately ± 22 meV. The significant differences observed in the parallel and perpendicular geometries indicate that the phonon density in the $L1_0$ -FePt has the pronounced anisotropy.

These observed phonon energy spectra include the contributions of not only the single phonon excitation process but also multiphonon excitation process and the elastic scattering (the intense central peak). Since only the contribution of the single phonon leads to the PDOS, it is necessary to remove the extra two contributions from the original spectra. The contribution of the elastic scattering by Mössbauer effect could be subtracted because the peak is represented by the Dirac delta function. The multiphonon contributions were also subtracted using an iterative procedure.¹⁵ Thus-obtained PDOS, which were determined by 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 revealed that the PDOS observed in 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). It suggests that the PDOS in $L1_0$ -FePt lattice along c axis has high probability at around 28 meV. In Fig. 3(b), the PDOS for the directions perpendicular to the c axis have the probabilities distributed from 17 to 32 meV. As mentioned above, the difference of spectra indicates that PDOS in the $L1_0$ -FePt has notable crystal anisotropy. These measurements also imply that the Debye temperature of the $L1_0$ -FePt along c axis is higher than that along the plane perpendicular to c axis. This can be ascribed to the chained structure with alternating Fe and Pt atoms, which have very different masses, located just along the c axis.

To confirm this result from a theoretical point of view, we performed first-principles calculations. We used the plane-wave projector augmented wave method¹⁶ as implemented in the VASP code^{17–19} and the generalized gradient approximation.²⁰ A plane-wave energy cutoff was chosen to be 300 eV. Phonon calculations were performed for the theoretically optimized structure of the $L1_0$ -FePt by the Parlinski-Li-Kawazoe method²¹ as implemented in the FROPHO code.^{22,23} Supercells of $2 \times 2 \times 2$ conventional unit cells with a set of finite atomic displacements by 0.01 Å were employed. Figures 3(c) and 3(d) show the results of the calculation along z axis and xy plane, respectively. Here z axis is defined as a direction parallel to the c axis in $L1_0$ -FePt. The contributions of directions perpendicular to the c axis such as (110) and (100) are mixed in the result of xy plane. The calculated PDOS along z axis shown in Fig. 3(c) consists of a strong peak at about 28 meV, which is consistent with the experimental result. On the other hand, the calculated PDOS along xy plane shown in Fig. 3(d) consists of two strong peaks at 18 to 24 meV. The calculated results also indicate that the PDOS in the $L1_0$ -FePt has the pronounced anisotropy.

We note that the orientation of c axis of the $L1_0$ -FePt nanoparticles in the composite has a finite distribution due to the thermal effect in the fixation process of the nanoparticles.

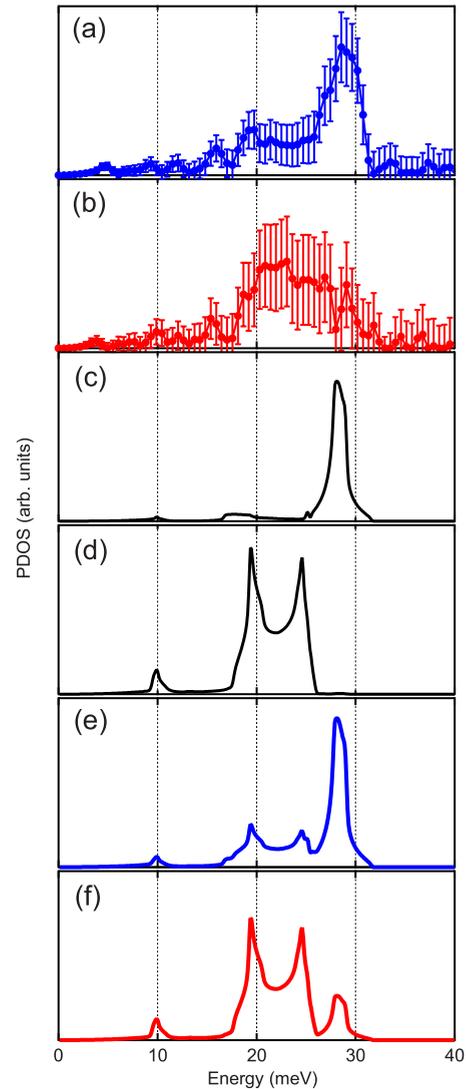


FIG. 3. (Color online) PDOS determined from the phonon energy spectra measured at 10 K in the (a) parallel and (b) perpendicular geometries. Theoretical PDOS along (c) z axis and (d) xy plane of the $L1_0$ -FePt in the bulk state calculated by the first-principles method for (e) parallel and (f) perpendicular geometries.

In order to reproduce the PDOS determined by measurement results, it is necessary to integrate the contribution of the calculated PDOS along z axis and xy plane with considering the distribution. Since the distribution of the c axis of the $L1_0$ -FePt nanoparticles was revealed in our previous work,¹² we can calculate the spectra expected to be observed in the parallel and perpendicular geometries.²⁴ The results are shown in Figs. 3(e) and 3(f), respectively. The computed PDOS of the parallel geometry shown in Fig. 3(e) is in good agreement with the experimental result [Fig. 3(a)]. The spectrum successfully reproduces the intensities not only at 28 meV but also from 16 to 26 meV. The other computed PDOS of the perpendicular geometry is shown in Fig. 3(f). It is also qualitatively in agreement with the experimental result [Fig. 3(b)]. We can see that the computed spectrum reproduces the intensities from 16 to 30 meV and a small peak at around 28 meV.

It should be pointed out that the first-principles calculations are made on $L1_0$ -FePt in the bulk state while the nanocrystals are actually employed in the experiments. It was reported by Fultz *et al.*²⁵ that the PDOS of ^{57}Fe metal had notable differences between bulk and nanocrystalline (approximately 10 nm) states, which was strongly enhanced at low energies below 15 meV. We consider that the minor difference between computed and experimental results can be originated from the effect of the smallness of the materials. It is therefore desirable to perform the inelastic scattering measurements of the $L1_0$ -FePt in the bulk state and compare it with the present results obtained from the nanocrystals (approximately 5 nm), which will be the subject of further study. We expect these studies would serve to clarify the characteristic lattice dynamics of nanoparticles.

In conclusion, we have studied the anisotropic PDOS of Fe atoms in the single-crystalline $L1_0$ -FePt nanoparticles. The nanoparticles were fixed in the polystyrene matrix with a strongly preferred orientation. The lattice dynamics was investigated using ^{57}Fe nuclear-resonant inelastic scattering of SR in SPring-8. The measurements were performed under

the condition that the incident x rays were parallel and perpendicular to the direction of the aligned c axis of the $L1_0$ -FePt nanoparticles. The PDOS along two directions were determined directly from the observed phonon energy spectra, which significantly differ from each other. It indicates that the PDOS in the $L1_0$ -FePt has the pronounced crystal anisotropy. To confirm this result from a theoretical point of view, we calculated PDOS along different directions in the bulk $L1_0$ -FePt by using the first-principles method. Considering the fact that the c -axis orientation of the $L1_0$ -FePt nanoparticles in the composite has the finite distribution, we computed PDOS expected to be observed under the experimental conditions. They were in good agreement with the PDOS determined by experimental results.

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