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Anisotropic lattice dynamics of FePt $L1_0$ thin films

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We employed nuclear inelastic scattering of synchrotron radiation to measure the anisotropy in the phonon density of states of an FePt thin film ordered in the $L1_0$ phase and compared our results with *ab initio* calculations. We find a strong anisotropy in the phonon density of states along the a and c axes of the crystal, which induces a difference in the calculated thermodynamic and elastic parameters along these axes. Calculations of surface-related effects show that a strong deviation from the bulk vibrational spectrum is observed for an Fe-terminated surface. We deduce by comparison with our surface sensitive measurement that the FePt(100)-oriented surface is Pt terminated. This contrasts with a recent measurement on FePt nanoparticles, where additional low-energy modes are observed. The findings are expected to be representative of the lattice dynamics of $L1_0$ intermetallics.

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I. INTRODUCTION

Intermetallic alloys ordering in the $L1_0$ crystal structure form a large class of technologically relevant materials for catalysis,[1] high-temperature mechanics,[2] and magnetic data storage.[3] In particular, FePt is one of the most promising candidates for ultrahigh density magnetic data storage technology.[3–6] One of the important issues for applications as perpendicular magnetic data-storage medium is the need to have its c axis perpendicular to the film plane, since this is the direction along which the magnetic easy axis is aligned. Along the c axis, an alternating stacking of Fe and Pt atomic sheets is found. Since the magnetic properties are intrinsically linked to the crystal anisotropy, fundamental questions regarding the formation and structural properties of this alloy in thin films need to be addressed.[7–9]

It is well known that anisotropic crystals, such as $L1_0$ intermetallics, exhibit an axial dependence of their physical properties.[10] While the anisotropy as such can be studied in bulk single crystals, it is most relevant to study its effect in thin films and nanostructures. In these geometries, the crystal anisotropy might interfere with the typically large surface-to-volume ratio of films and nanoparticles. Finite size and, in particular, surface effects might become predominant. The study of atomic vibrations, in solids described by the phonon density of states (PDOS), can provide key information to understand the basic mechanical properties and the phase stability of the alloy, since it allows to access elastic (mean force constant, mean displacement) and thermodynamic (heat-capacity, vibrational entropy) parameters, which influence the movement of atoms. The anisotropic behavior of these parameters can be accessed by probing the anisotropic vibrational properties of the crystal, i.e., by resolving the PDOS projected onto selected axes. A few phonon studies (experimental or theoretical) on the $L1_0$ structure have been reported in literature.[8,11,12] Very recently, the anisotropic behavior of the phonon density of states of FePt ordered in the $L1_0$ structure has been reported for FePt *nanoparticles* using nuclear inelastic scattering.[13] However, the spread in relative orientations of the nanoparticles did not allow a direct disentanglement of the a- and c-axes-projected phonon density of states. The authors also point to the influence of surface vibrations (which might be predominant in nanoparticles) as a source for the appearance of additional low-energy vibrational modes. The lack of a similar study carried out on FePt single crystal prevented a clear conclusion on their results.

In this paper, we present a combined experimental (using nuclear ineastic scattering) and theoretical (by *ab initio* calculations) study of the anisotropy in the phonon density of states of FePt thin films. The use of *epitaxial thin films* allows us to extract the phonon density of states projected onto the a and c axes and compare to theoretical predictions. The influence of strain, which is important for epitaxial films as well as for nanoparticles, is highlighted. Finally, the influence of surfaces on the phonon modes is discussed, both experimentally and theoretically, and this allows to derive conclusions on possible phonon softening in $L1_0$ intermetallics.

II. EXPERIMENTAL DETAILS AND SAMPLE PREPARATION

In the case of FePt, probing the anisotropic PDOS using a standard technique like inelastic neutron scattering proves to be impossible due to the lack of *bulk* single crystals. However, highly ordered FePt *thin films* can be epitaxially grown on proper substrates.[14,15] The thin-film geometry can be investigated by the nuclear inelastic scattering (NIS) (Ref. 16) technique, which is based on the excitation by synchrotron radiation of an extremely sharp ($<\mu$eV) nuclear resonance of specific Mössbauer isotopes, such as ^{57}Fe. The large nuclear cross section of the ^{57}Fe resonance allows one to study the PDOS of ^{57}Fe thin films down to the single-atomic-layer regime.[16] The probability of exciting a phonon shows a

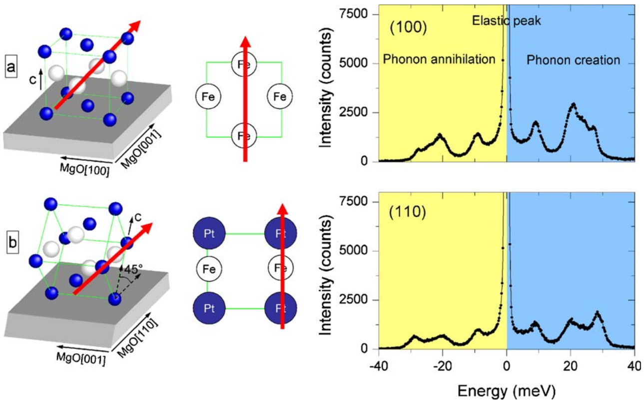

FIG. 1. (Color online) The left schematic illustrates the orientation of the FePt lattice grown on (a) MgO(100) and (b) MgO(110) substrates. The red arrow indicates the direction of the x-ray beam. The corresponding nuclear inelastic spectra, recorded at 300 K, are displayed on the right panels for both orientations.

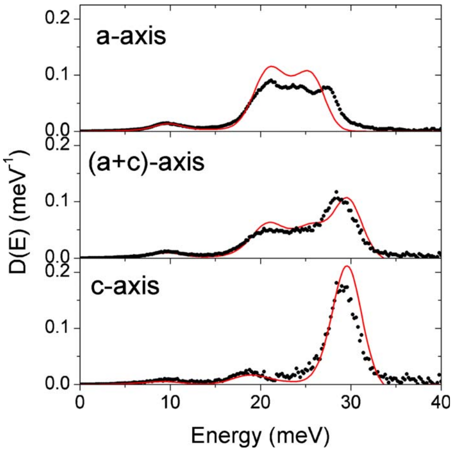

FIG. 2. (Color online) Fe partial phonon densities of states along the different crystalline axes. The solid lines are *ab initio* calculations using an artificially strained lattice convoluted with a Gaussian distribution accounting for the experimental broadening.

$|\boldsymbol{k_0}\cdot\boldsymbol{e_j}|^2$ dependence, where $\boldsymbol{k_0}$ is the photon wave vector and $\boldsymbol{e_j}$ is the polarization vector of vibration along the $j=a,b,c$ crystalline axes.[17] Consequently, one measures the projection of the phonon states on the axis defined by the x-ray beam.

To probe both the a- and c-axes projection of the PDOS, the x-ray beam has to be aligned along two nonequivalent crystalline axes while maintaining the grazing incidence geometry. This is achieved by growing simultaneously 30-nm-thick ^{57}FePt films on a MgO(100) and a MgO(110) substrate (placed on the same holder) by molecular-beam epitaxy coevaporation of ^{57}Fe (from an effusion cell) and Pt (from an electron-beam source) at a substrate temperature of 500 °C. The growth rate was set to 0.0027 nm/s and 0.0035 nm/s for ^{57}Fe and Pt, respectively. The different epitaxial relations between FePt and the respective substrates lead to the c axis being oriented out of plane for the FePt(100) sample while the FePt(110) sample has its c-axis-oriented 45° out of plane and along the (110) in-plane directions of the substrate,[18] as illustrated in Fig. 1. The epitaxial growth is confirmed by x-ray diffraction measurements from which we also derive lattice constants of $a=0.385$ nm and $c=0.371$ nm for both samples. The latter value is smaller than for bulk FePt ($c=0.377$ nm) (Ref. 18) indicating a small strain of the crystal. The exact composition of the alloy was checked by Rutherford backscattering spectrometry to be $Fe_{0.49}Pt_{0.51}$. Conversion electron Mössbauer spectroscopy confirmed the easy axis of magnetization to be 90° and 45° out of plane for the FePt(100) and FePt(110) samples, respectively.

III. RESULTS

A. Nuclear inelastic scattering

We carried out room-temperature nuclear inelastic scattering experiments at the ID18 nuclear resonance beamline[19] of the ESRF (Grenoble, France). The spectra were recorded in grazing incidence geometry at an incident angle of 0.26°. As this angle is smaller than the critical angle of total reflection of FePt (0.33° at 14.4 keV), more than 25% of the signal originates from the upper first nanometer of the FePt layer. This means that the experiment will be highly sensitive to surface effects, as will be discussed later. The recorded energy dependence of the nuclear scattering cross sections, referenced hereafter as NIS spectra, is shown in Fig. 1 for both orientations.

The phonon densities of states were extracted from the NIS spectra using the DOS software.[20] To extract the c-axis PDOS, one has to decompose the contribution of the a and c axes from the $(a+c)$-axis PDOS.[17] Since the PDOS cross term vanishes in case of tetragonal symmetry, we can write

$$\mathrm{DOS}(a+c) = \mathrm{DOS}(a)\cos^2(45°) + \mathrm{DOS}(c)\cos^2(45°)$$

from which the c-axis-projected DOS can be extracted. The results are shown in Fig. 2. The most striking features of the c-axis PDOS are the decreased intensity of the low-energy modes compared to the a axis and the presence of mainly one peak at 29 meV. From the obtained PDOS, we calculated the orientation dependence of various thermodynamic and elastic properties which are listed in Table I. It should be noted that these values represent only the properties of the Fe atoms in the alloy.

One sees that the crystal anisotropy leads to relatively large variations in the listed quantities, especially the mean interatomic force constant, mean atomic displacement, and the vibrational entropy S_{vib} display large variations. This an-

TABLE I. Parameters extracted from the measured phonon density of state for the different crystalline axes.

	a	$a+c$	c
Physical quantity	(100)	(110)	(010)
Specific heat (k_B/atom)	2.78(1)	2.76(1)	2.73(1)
Vibrational entropy (k_B/atom)	3.52(1)	3.31(1)	3.12(1)
Mean atomic displacement (Å)	0.075(1)	0.073(1)	0.072(1)
Mean force constant (N/m)	129.6(4)	142.9(4)	159.2(4)
Mean sound velocity (m/s)	2214(20)	2101(20)	2016(20)

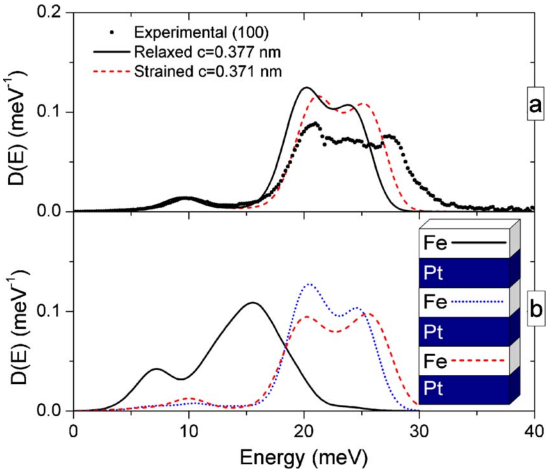

FIG. 3. (Color online) (a) *Ab initio* calculations of the bulk PDOS of the Fe atoms for a fully relaxed FePt(100) crystal structure and for the artificially strained case, where the lattice parameters match the experimental ones. (b) Surface effect calculations. Only the Fe-terminated surface (solid line) shows strong deviations from the bulk behavior. The calculated PDOS have been convoluted with a Gaussian distribution accounting for the experimental broadening.

isotropic behavior may thus play a role in the thermodynamic stability of such alloy.

B. *Ab initio* calculations

To obtain a deeper insight in the lattice dynamics of FePt, we performed first-principles phonon calculations. The *ab initio* calculations for the bulk $L1_0$ FePt were performed on a $4\times4\times3$ supercell (containing 96 atoms) with periodic boundary conditions. The crystal-structure optimization and calculations of Hellmann-Feynman forces were performed with the first-principles VASP package[21] and using the spin-polarized density-functional total-energy formulation with general gradient approximation. Iterative optimization of the supercell structure was terminated when residual interatomic forces decreased below 10^{-5} eV/Å and stresses were less than 0.1 kbar. The phonon frequencies were determined with the direct method,[22] which makes use of the Hellmann-Feynman forces obtained when small atomic displacements from equilibrium positions are applied. Subsequently, the dynamical matrix was constructed, diagonalized for a large set of wave vectors, and the PDOSs were calculated for all relevant experimental conditions. After optimization, we obtained (bulk) lattice parameter values equal to $a=0.386$ nm and $c=0.377$ nm. In order to account for the experimental resolution (0.8 meV) and the broadening of the vibrational states induced by the finite lifetime of the phonons, the calculated PDOS have been convoluted with a Gaussian distribution of 6 meV full width half maximum. The PDOS obtained from the *ab initio* calculations for the fully relaxed crystal on the FePt(100) direction yields a spectrum which is shifted to lower energies compared to the experiment, as shown in Fig. 3(a). Since we have determined an experimental value of $c=0.371$ nm in our sample, we carried out further *ab initio* calculations for a strained structure, which assumes the same lattice constants as derived from x-ray diffraction. These calculations yield a PDOS with peaks at similar energies as in the experiment. The results of the calculations for the different axes shown in Fig. 2 are in good agreement with the measured PDOS. An important remark is that the smaller c-axis lattice parameter shifts the PDOS projected onto *both* axes. The shift of the PDOS which we observe in the calculation indicates that the PDOS is very sensitive to the lattice spacing and, in turn, to the elastic strain in the sample. One can calculate that, due to the strain, the vibrational entropy increases by $0.2k_B/\text{atom}$ for the a-axis-projected PDOS. This leads to an increase in the system energy of 0.026 eV/atom (at 300 K), which have to be compared to the change in enthalpy (due to the volume reduction) which is estimated around 0.58 eV per atom. The contribution originating from the vibrational entropy may therefore be significant for the system's internal energy. Future studies of the role of strain induced by different layer/substrate epitaxy would allow to determine to which extent strain engineering can be used to tailor the lattice dynamics of $L1_0$ intermetallic compounds.

C. Surface effects

The grazing incidence geometry of the NIS experiment leads to an extreme surface sensitivity. Hence, the PDOS that we record is likely to be affected by surface effects, due to the asymmetric bonding or to varying lattice parameters. We performed further calculations for a slab composed of three Fe/Pt atomic bilayers [simulating the (100)-oriented sample] with free surfaces perpendicular to the c axis. The PDOS obtained for each of the individual Fe layers is shown in Fig. 3(b). Only for the surface Fe layer, the PDOS differs significantly from the bulk one. The second Fe layer [dotted line in Fig. 3(b)] and the case of a Pt-terminated surface [dashed line in Fig. 3(b)] show a bulklike spectrum. We estimate in the case of an Fe-terminated layer that about 10% of the signal would originate from that very first layer. Since we do not observe any additional low-energy modes in the PDOS, we can deduce that the FePt layer is Pt terminated. This is in agreement with recent work on surface-energy calculations of FePt and CoPt alloys.[23] The extreme surface sensitivity of the PDOS was already observed for metallic Fe grown on W(110).[16] The FePt alloy behaves in a similar manner: already starting from the second atomic layer, a bulklike vibrational spectrum appears. We therefore expect that the dynamics of a thinner layer or of FePt nanoparticles will remain close to the bulk properties. In fact, according to our findings, even nanoparticles, if they are Pt terminated, should show a vibrational spectrum (of the Fe atoms) very similar to the bulk one. Recently, a NIS study carried out on oriented FePt nanoparticles revealed an increased number of low-energy modes, which was attributed to the small size of the particles (5 nm). According to our result on thin films, which resemble "bulk" crystals, the appearance of low-energy modes can only be explained by the appearance of Fe-terminated surfaces (which show the low-energy modes). The question whether the low-energy modes observed in nanoparticles indeed originate from such Fe surfaces rather than pure confinement effect should be investigated in more detail. It would eventually mean that the formation of an Fe-terminated surface is favored in nanoparticles while it is not the case in thin films. The question of surface termination in FePt nanoparticle can have important consequences for the fabrication, stability, and properties of FePt nanoparticles which are foreseen to be used in future high-density magnetic recording media.

IV. CONCLUSION

In conclusion, we have measured the anisotropy in the phonon density of states of FePt thin films ordered in the $L1_0$ structure. We expect that the main features of the anisotropic PDOS are not limited to FePt but are representative of the $L1_0$ intermetallic alloys. We see that the *a*-axis projected vibrations incorporate several low-energy modes and that the *c*-axis PDOS shows mainly one mode at 29 meV complemented with less pronounced low-energy modes. The results are compared with *ab initio* calculations, which reproduce very well the measured spectrum if one takes the epitaxially induced elastic strain into account in the calculations. The phonon anisotropy originates from anisotropic thermodynamic and elastic properties (e.g., the elastic constants). The orientation dependence of these quantities has been extracted and shows up to 10% variations. Surface effects were theoretically investigated, showing that only the top atomic layer has a vibration spectrum deviating from the bulk case. This latter finding, in combination with our experimental data, allows us to conclude that the FePt(100) layer is Pt terminated. This seems to be in contrast with a recent NIS study of FePt particles, where increased low-energy modes were observed. We believe that the different behavior of the thin film compared to the nanoparticles could be due to a modification of the stability of the alloy in the case of the nanoparticles, an effect that deserves further investigation. The presented findings reveal a particular anisotropic behavior which is important for further magnetoengineering of $L1_0$ intermetallic bulk alloys and nanoparticles.

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