**Experiment title:**
Phonon density of states in bimetallic epitaxial metastable thin films

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**Introduction**

The use of vacuum-deposited ultrathin films has already led to big advances, e.g. in the actuator industry and the data storage technology. In the future, the possibility to stabilize new metastable materials via the epitaxial growth may lead to the discovery of yet unknown phenomena and revolutionary applications. The possibility to make new metastable bimetallic materials is quite inexhaustible, and its exploration took off only in recent years. The low growth temperature and atomic layering capability allows to obtain complex structures, referred to as digital alloys or monoatomic superlattices.

In condensed matter studies of novel materials, the knowledge of the dynamics of the atomic motion is very valuable. The dynamical properties are embodied in the phonon density of states (PDOS), from which one can deduce the thermodynamic properties like the free energy, the entropy, the heat capacity, the thermal expansion or the heat conductivity. In systems of reduced dimension, it is expected that the presence of surfaces and interfaces will also influence the electronic and thermal properties. However, in ultra thin films, it is difficult to probe the PDOS by established methods like neutron inelastic scattering. Therefore, we proposed to probe the site-selective PDOS of bimetallic metastable epitaxial systems via nuclear inelastic scattering of synchrotron radiation in prototypical structures, namely, in metastable [Feₘ/Auₙ] mono-atomic multilayers, in metastable CsCl-structured FeSi layers, and in metastable bcc-FeCo thin films. The phonon density of states of the metastable structures can be compared to the one of the stable counterparts. The aim of the study is to measure the PDOS and to compare the results with *ab-initio* calculations.

1. **Theoretical calculations on the vibrational density of states**

The [Feₘ/Auₙ] superlattices [1] can be engineered by alternative layer by layer deposition of m Fe and n Au atomic layers, N times repeated. In the mono-layer limit (m=n=1), a tetragonal L1₀ (AuCu-type) structure can be fabricated, which does not exist naturally in the Fe-Au phase diagram. The multilayers exhibit attractive magnetic properties, combining perpendicular magnetic anisotropy with high magnetic moments. Despite intensive theoretical [2-5] and experimental [4-7] studies, the understanding of the condition for the formation of long-range chemical order in the Feₙ/Auₙ multilayers and also the local structure and stability of systems Feₘ/Auₙ for n,m ≤ 5 is still lacking. Using ab-initio methods, we found the minimal ground-state energy for various Feₘ/Auₙ structures, and we calculated the phonon dispersion relations and the PDOS spectra, as described in a related Dynasync paper [8]. The phonon calculations indicated that a relaxation of
atomic positions from tetragonal symmetry is necessary for certain to get the stable configuration. The calculated PDOS showed to be extremely sensitive to the multilayer structure, as exemplified in Fig.1 for unrelaxed structures. The deviation from bulk behavior is striking, and the system should allow us to investigate the influence of magnetic order on the lattice dynamics, since the magnetic ordering can be triggered by tuning the superlattice periodicity.

The metastable CsCl-FeSi phase does not occur in nature, but may be stabilized by the epitaxial growth on a suitable substrate. Thus, the electronic and magnetic properties can only be studied in thin films. This system attracts much interest nowadays because of interlayer coupling related phenomena [10]. We performed an ab-initio studies of the interlayer coupling and of the PDOS in Fe/FeSi multilayers [11]. The studies indicated a strong difference between the PDOS for Fe in the FeSi spacer layer, for Fe at the Fe/FeSi interface, and for Fe in the Fe layers.

Fig. 1: Selection of the phonon density of states spectra for the different Fe/Au multilayers. The lines and the shaded areas describe the total density of states and the Fe partial density of states, respectively.

The density of states for Fe within the FeSi layer has a maximum at $\omega = 4.5$ and one at $\omega = 7.2$ THz, and appreciable intensity in between for the $X$-$Y$ phonon polarization. The Z polarized phonon spectrum has quite different shape, however it is not accessible by the nuclear inelastic scattering experiment. One should also notice that the phonon spectra vary for different Fe layers depending how far away is the layer from the Fe/FeSi interface.

2. Sample preparation

Metastable Fe$_m$/Au$_n$ mono-atomic superlattices were prepared at ICSC Krakow by alternating deposition of Au$_m$ and $^{57}$Fe$_n$ layers on the Au(001) buffer layer grown on polished MgO(001) substrate. The symbols $m$ and $n$ denote the number of Au(001) and Fe(001) monolayers respectively. The obtained superlattices, [Au$_1$Fe$_1$]$_{15}$, [Au$_2$Fe$_2$]$_{10}$, [Au$_3$Fe$_3$]$_{7}$, [Au$_2$Fe$_1$]$_{15}$, [Au$_1$Fe$_1$]$_{15}$, were finally capped with thin Au protective layer to enable ex-situ characterization. The high quality low energy electron diffraction patterns observed at every preparation step, starting from the Au buffer to the top capping layer, confirmed the epitaxial structure of the systems. Conversion electron Mössbauer spectroscopy (CEMS) was used to check the local structural and magnetic order in the superlattices. Numerical analysis of the [Au$_1$Fe$_1$]$_{15}$ CEMS spectrum clearly showed imperfect sample stacking related most probably to the Au segregation process. The fraction the Fe atoms in the ideal [Au$_1$Fe$_1$]$_{n}$ structure contributing to the sub-spectrum with a high quadruple splitting (green line in the top spectrum) can be estimated to about 30%. The other components are related to the double-layer patches and iron atoms in an Au-Fe substitutional alloy. The relative line intensities in the Zeeman sextets indicated perpendicular magnetic anisotropy of the [Au$_1$Fe$_1$]$_{15}$ sample, confirmed by ex-situ Magneto-optic Kerr Effect (MOKE) measurements. In case of [Au$_3$Fe$_3$] multilayer the atomic structure derived from the CEMS data is much closer to the nominal one. In addition, the in-plane magnetic anisotropy could by concluded for this system in agreement with MOKE investigations.

We have stabilized CsCl-type FeSi layers in Fe/FeSi multilayers via the epitaxial growth on MgO substrates [9]. In the CsCl-type films, our past investigations revealed a strain relaxation with increasing
layer thickness. The tetragonal strain in the FeSi spacer layer reduces from 7% when the FeSi spacer is less than 2 nm to 3% for relatively thick layers of 8 nm [9]. Complementary to the CsCl-FeSi films, we also produced stable ε-FeSi thin films for comparison. The conversion electron Mössbauer spectrum of the ε-FeSi thin film is characterized by an isomer shift of 0.2448(12) mm/s and a quadrupole splitting of 0.5265(21) mm/s.

Metastable FeCo thin films were also grown on MgO(100) substrates. Depending on the Fe concentration, a different growth procedure is chosen to obtain the bcc Co phase. A first series of samples exists of one Fe<sub>x</sub>Cox layer of 50 nm, directly deposited on MgO. It is shown that these samples have the bcc phase if the iron concentration is larger than 20%. For lower iron concentrations, the bcc phase of pure Co layers are stable for thickness t between 0.8 nm and 2.1 nm. Therefore FeCo layers with a low Fe concentration of 1.7 nm thickness are grown repeatedly on pure Fe layers. These Fe/FeCo bilayers are repeated 20 to 40 times to increase the amount of <sup>57</sup>Fe in the samples. XRD spectra on an epitaxial bcc-Fe<sub>0.02</sub>Co<sub>0.98</sub> periodic multilayer and an fcc-Fe<sub>0.02</sub>Co<sub>0.98</sub> thin film are obtained (not shown). The scans clearly show the MgO(200) substrate peak, the bcc-FeCo(200) diffraction peak around 65° (left) or a diffraction peak around 51° (right). The latest peak can be allocated to the fcc-FeCo.

3. Nuclear Inelastic Scattering of Synchrotron Radiation

The method of inelastic nuclear scattering of synchrotron radiation (NIS) to measure the phonon density of states on the <sup>57</sup>Fe isotopes was introduced in 1995 by Seto [12] and Sturhahn [13]. In the meantime, it was demonstrated that the technique also allows to probe the phonon density of states of impurity atoms in alloys [14], and of nanosize precipitates and clusters [15]. We performed the inelastic nuclear scattering of synchrotron radiation experiments at the ID18 beamline of the ESRF with a high-resolution monochromator (2.0 meV) in the period of February 2-6, 2007. An energy range of ±70 meV was scanned in steps of 0.5 meV. The main experimental results of room temperature measurements are presented in Figure 3.

![Fig. 3: Partial phonon density of states (g(E)) for various mono-atomic FeAu multilayers (left), for CsCl-type FeSi compared to ε-type FeSi (middle), and for bcc FeCo compared to fcc FeCo thin films (right).](image-url)

It can be clearly seen that vibrational properties of iron atoms in the (Fe<sub>1</sub>Au<sub>1</sub>)<sub>15</sub>, (Fe<sub>1</sub>Au<sub>3</sub>)<sub>15</sub> multilayers are similar, and they are significantly different from (Fe<sub>3</sub>Au<sub>3</sub>)<sub>7</sub>. The increased intensity of high energy modes in VDOS of (Fe<sub>3</sub>Au<sub>3</sub>)<sub>7</sub> as compared to (Fe<sub>1</sub>Au<sub>1</sub>)<sub>15</sub> and (Fe<sub>1</sub>Au<sub>3</sub>)<sub>15</sub> can be correlated with a disappearance of the low energy peak clearly seen in the multilayers with the Fe monolayer, in agreement with the theoretical calculations. The direct comparison of the measured and calculated DOS is shown in Fig. 4. The theoretical spectra were convoluted with the instrumental function. For the (Fe<sub>3</sub>Au<sub>3</sub>)<sub>7</sub> agreement between theory and experiment is fairly good. It reflects the stability of the non-relaxed structure formed by the repeated stack of three Fe(001) and three Au(001) monolayers. The ideal L<sub>1</sub> structure, formed by the repeated stack of one Fe(001) and one Au(001) monolayer is thermodynamically unstable. In the real structure there is only a short range L<sub>1</sub> order. This explains a small intensity of the characteristic phonon peak around 30 meV. Despite apparent differences between the theoretical and experimental data, all characteristic phonon peaks at 10 meV, 18 meV and 30 meV can be identified in the experimental spectrum. The dominating peak at 23 meV arises from sample regions deviating from the perfect Fe<sub>1</sub>Au<sub>1</sub> structure, where Fe forms clusters or double and tree-layer nano-structures.

We have also found that for the (Fe<sub>3</sub>Au<sub>3</sub>)<sub>15</sub> multilayer (Curie temperature below RT), the phonon DOS does not change under magnetic transition, down to 100 K.
Fig. 4: Partial phonon density of states g(E), projected to the photon propagation direction (the layer plane) for various mono-atomic FeAu multilayers compared with the calculated partial phonon DOS’s with vibrations in the (001) plane. Dashed lines and solid lines are for non-relaxed and relaxed structures, respectively.

The dramatic difference, in figure 4, between the phonon density of states for CsCl-FeSi and ε-type FeSi is even more apparent when inspecting figure 5, in which the reduced phonon density of states of CsCl-type FeSi layers is compared to ε-FeSi. In this representation strict Debye-like behavior is reflected by a horizontal line. More detailed investigations will be needed to gain further insight into this behaviour.

Fig. 5: Reduced phonon density of states for CsCl-type FeSi and ε-type FeSi compared to bcc-Fe.

The spectrum of phonon density of states for bcc-type FeCo (fig 3, right panel) drastically differs from the one of fcc-type FeCo with the same concentration. Qualitatively, this can be understood from the different coordination number for Fe in the two differing crystal structures. Indeed, the bcc structure is more densely packed, thus yielding a higher phonon density of states at relatively higher energies. Again, the experimental results will be compared to a detailed theoretical study to gain more insight.

Conclusion

We performed a direct comparison of the theoretical and experimental phonon density of states in artificial low dimensional systems. The importance of studying the phonons to define the phase stability conditions is being demonstrated by the state of the art approach – namely by comparing the experiment with first principle theory.

References