Element-resolved thermodynamics of magnetocaloric LaFe$_{13-x}$Si$_x$

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Abstract

By combination of two independent approaches, nuclear resonant inelastic X-ray scattering and first-principles calculations in the framework of density functional theory, we determine the element-resolved vibrational density of states in the ferromagnetic low temperature and paramagnetic high temperature phase of LaFe$_{13-x}$Si$_x$. This allows us to derive the lattice and electronic contribution to the entropy change at the first-order phase transformation, which are both of considerable magnitude. The change in lattice entropy is dominated by magnetoelastic softening, which originates from the itinerant electron metamagnetism associated with Fe. This counteracts the large volume change at the transition and leads to an unexpected, cooperative behavior of magnetic, vibrational and electronic entropy change, which is responsible for the large magneto- and barocaloric effect observed for this material.

PACS numbers: 75.30.Sg, 63.20.-e, 71.20.Lp, 76.80.+y

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Ferroic materials allow for significant adiabatic temperature changes induced by realistic electrical and magnetic fields, by external stress and under pressure [1–4]. This allows their use in solid state refrigeration concepts as an energy efficient alternative to the classical gas-compressor scheme. A good cooling material is characterized by a large isothermal entropy change $|\Delta S_{iso}|$, which determines the latent heat to be taken up during a first-order transformation in conjunction with a high adiabatic temperature change $|\Delta T_{ad}|$. Apart from the prototype Gd-based systems [5], a large number of suitable materials were proposed, which undergo a magnetic first-order transition and perform well in both respects (e.g., [6]). Among the outstanding materials are LaFe$_{13-x}$Si$_x$-based systems ($1.0 \leq x \leq 1.6$) [7–9], which consist of largely abundant components [3]. Their structure corresponds to cubic NaZn$_{13}$ ($Fm\bar{3}c$, 112 atoms in the unit cell), with two crystallographically distinguished Fe-sites, Fe$_I$ and Fe$_{II}$, on the 8-fold (8b) and 96-fold (96i) Wyckoff-positions, respectively. La resides on (8a)-sites, while Si shares the (96i) site with Fe$_{II}$ [10–12]. The Curie temperature, $T_C$, of the ferro- (FM) to paramagnetic (PM) transformation is around 200 K, depending on composition. $T_C$ increases proportionally with increasing Si-content [13, 14], but the transition changes to second-order, while $|\Delta S_{iso}|$ and $|\Delta T_{ad}|$ decrease significantly. By concomitant hydrogenation and Mn substitution, $T_C$ can be precisely adjusted to ambient conditions without severe degradation of the caloric performance [15–18]. The first-order magnetic transformation is accompanied by an abrupt volume decrease of 1% for $x = 1.5$ upon the loss of magnetic order [19]. This also gives rise to a large inverse barocaloric effect [20]. In the FM phase the thermal expansion coefficient is largely reduced or even negative [10, 21], which presents similarities with the Invar-type thermal expansion anomalies discovered in Fe$_{65}$Ni$_{35}$ (and other ferrous alloys) more than one hundred years ago (e.g., [22]).

Consequently, the moment-volume-instability of La-Fe-Si has been discussed in terms of the itinerant electron metamagnetism (IEM) arising from the (partially) non-localized character of the Fe moments [23, 24] within a phenomenological Ginzburg-Landau description [25, 26]. The IEM picture gained further support from first-principles calculations [27–29] through the identification of metastable minima of the binding surface, which correspond to metastable magnetic configurations at distinct volumina. This is also a characteristic feature of Fe-Ni Invar, where the compensation of thermal expansion is linked to the redistribution of charge between non-bonding majority spin-states above and anti-bonding minority spin states below the Fermi-level [30]. However, further ab initio work on La-Fe-Si concentrates
on the electronic structure in the FM phase and the non-spinpolarized state \cite{25, 31, 33}, while thorough characterization of the paramagnetic phase is still missing.

In this letter we will establish the link between the electronic structure of La-Fe-Si and its macroscopic thermodynamic behavior in both, the FM and the PM phase, by a combination of nuclear resonant inelastic X-ray scattering (NRIXS) and \textit{ab initio} lattice dynamics. We disentangle the elemental contributions to the vibrational density of state (VDOS), which determines the intrinsic vibrational thermodynamic properties, such as lattice entropy, and relate them to phase-induced changes in the electronic structure.

The isothermal entropy change is usually divided up as $\Delta S_{\text{iso}} = \Delta S_{\text{mag}} + \Delta S_{\text{lat}} + \Delta S_{\text{el}}$, i.e., into the contributions from the magnetic, lattice and electronic degrees of freedom, respectively \cite{1}. These are associated with the configurational entropy arising from spin disorder, excitation of quasi-harmonic phonons and thermal occupation changes of the electronic states, respectively. Mixed interactions are often not taken into account separately, although they might enhance $\Delta S_{\text{iso}}$ significantly \cite{31} and can be expected for 3$d$ metals \cite{1}. Anharmonic contributions are neglected here as well. For La-Fe-Si, $\Delta S_{\text{mag}}$ is expected to be the driving contribution, while $\Delta S_{\text{el}}$ is considered negligible and $\Delta S_{\text{lat}}$ is deemed to counteract assuming a quasiharmonic renormalization of the Debye temperature $\Theta$ \cite{14, 35}.

In the following we will demonstrate, that both, $\Delta S_{\text{lat}}$ and $\Delta S_{\text{el}}$ contribute \textit{cooperatively} to the magnetocaloric effect. The sign of $\Delta S_{\text{lat}}$ is determined by the IEM of Fe, which affects magnetoelastic interactions and thus modifies phonon frequencies oppositely to what is expected from Grüneisen theory.

For the measurements, a 5 g ingot of material with nominal composition LaFe$_{11.6}$Si$_{1.4}$ was produced by arc-melting in pure Ar atmosphere. 10\,wt.-\% of the stoichiometric portion of iron was replaced by the $^{57}$Fe isotope of 95\,\% in isotopic enrichment. To stabilize the cubic La(Fe,Si)$_{13}$-phase, the ingot was annealed for 7 days at 1323 K followed by quenching in water. The sample was characterized by X-ray diffraction and 14.4-keV Mössbauer backscattering spectroscopy \cite{39}, showing that 89 $\pm$ 1\,\% of the Fe atoms in the sample are in the La(Fe,Si)$_{13}$ phase. 11 $\pm$ 1\,\% are in the bcc Fe secondary phase, which occurs unavoidably at small Si contents \cite{9, 18}. Magnetization measurements reveal in agreement with \cite{7} a first-order FM-PM transition at $T_C = 189$ K with a hysteresis of 3 K. NRIXS \cite{37, 39} was performed at Sector-3 beamline at the Advanced Photon Source, Argonne National Laboratory. The incident X-ray energy was around $E_0 = 14.412$ keV, the nuclear resonance energy
FIG. 1: (Color online) Element-resolved vibrational density of states of FM and PM LaFe$_{1-x}$Si$_x$. Orange circles with error bars denote the partial $^{57}$Fe-DOS obtained with NRIXS at $T_{\text{exp}} = 62$ K and $T_{\text{exp}} = 299$ K, respectively, corrected for the bcc Fe secondary phase contribution \[36\]. The lines refer to the DFT results for different magnetizations ($M = 24.5\mu_B/\text{f.u.}$ and $M = 3.75\mu_B/\text{f.u.}$, respectively). The thick red lines denote the partial DOS of the Fe atoms, which compares to the NRIXS measurement. The thinner black, the green dotted and the blue dash dotted lines refer to the total VDOS and the partial contributions of Si and La, respectively.

The X-ray beam is highly monochromatized with an energy bandwidth of 1 meV using a high-resolution crystal monochromator \[40\]. NRIXS was carried out in zero external magnetic field at four different measurement temperatures $T_{\text{exp}}$, two in the FM phase (62 K, 164 K) and two in the PM phase (220 K, 299 K). The $^{57}$Fe-specific VDOS were extracted from the NRIXS data using the PHOENIX program \[41\] and corrected for the $\alpha$-Fe contribution \[36\].

The \textit{ab initio} part is carried out with the VASP package \[42, 43\] in the framework of density functional theory (DFT) using the generalized gradient approximation (GGA) \[44\]. We represented the 112 atom unit cell with cubic basis vectors by a 28 atom primitive cell with fcc basis and introduced three Si atoms on the (96i) sites, i.e., $x = 1.5$ Si per formula unit (f.u.),
such that the space group is minimally reduced to rhombohedral \((R3)\) with still 12 inequivalent lattice sites. For the PM phase, we carefully selected a stable collinear spin arrangement with 10 inverted Fe moments. This yields a total spin-magnetization of \(3.75 \mu_B/\text{f.u.}\) compared to \(24.5 \mu_B/\text{f.u.}\) for FM. An average spin-moment of \(1.7 \mu_B/\text{Fe}\) was obtained for PM as compared to \(2.2 \mu_B/\text{Fe}\) for FM in good agreement with available Mössbauer, neutron diffraction and DFT data \([12, 13, 28, 45]\). The structures were carefully optimized with respect to cell shape, volume and atomic positions before the dynamical matrix was constructed with Dario Alfè’s PHON code \([46]\) based on the Hellmann-Feynman forces obtained from 56 individual \(\pm\)-displacements in a \(2\times2\times2\) supercell. This yields the vibrational density of states (VDOS), \(g(E)\), from which we obtain access to thermodynamic quantities like the lattice entropy \(S_{\text{lat}}\) and their temperature dependence \([47, 48]\). Similar first-principles calculations for \(\text{Ni}_2\text{MnGa}\) have reached excellent agreement between theory and experiment \([49, 50]\). In this work, we restrict to the harmonic approximation using the equilibrium volume of both magnetic states since we do not expect significant changes in \(g(E)\) from thermal expansion below and immediately above \(T_C\). For further experimental and computational details, see the supporting information \([36]\).

All distinct features of the partial VDOS of Fe obtained with NRIXS from the \(\text{La(Fe,Si)}_{13}\) phase are well reproduced by DFT (Fig. 1). This justifies our structural model for both phases and verifies our La and Si partial and the total VDOS, which we can only obtain from DFT. Changes between the FM and the PM phase arise mainly from a broadening of the La peak at 12 meV and the removal of the Fe peaks at 29 meV and 38 meV, while the other features related to Fe are uniformly shifted to lower energies. Thus, we encounter an overall softening in \(g(E)\) upon heating, which overrides the stiffening expected from Grüneisen theory, according to the volume contraction. From the NRIXS \(g(E)\) we obtain the temperature dependent lattice entropy \(S_{\text{lat}}(M, V)\) corresponding to volume \(V\) and magnetization \(M\) at the respective \(T_{\text{exp}}\) using a textbook relation \([48]\). Fig. 2 shows that changing from FM to PM state at \(T_C\) results in an increase in \(S_{\text{lat}}\), which amounts to \(\Delta S_{\text{lat}}^{\text{Fe}}|_{T_C} = 11 \text{ J kg}^{-1}\text{K}^{-1} = 0.10 \text{ k}_B/\text{Fe}\) calculated from the NRIXS VDOS for \(T_{\text{exp}} = 62 \text{ K}\) and 299 K. This is about one half of \(\Delta S_{\text{iso}} = 24 \text{ J kg}^{-1}\text{K}^{-1}\) from literature \([7]\). From the NRIXS data at \(T_{\text{exp}} = 164 \text{ K}\) and 220 K we obtain \(\Delta S_{\text{lat}}^{\text{Fe}}|_{T_C} = 5 \text{ J kg}^{-1}\text{K}^{-1}\), since in the vicinity of \(T_C\), increasing spin disorder in the FM phase and the remaining FM correlation in the PM phase reduce the entropy change. The entropy Debye temperature, \(\Theta_S\), derived from the logarith-
FIG. 2: (Color online) Total (left scale) and Fe-contribution (right scale and inset) to the lattice entropy and electronic entropy of the FM and PM phases. For a Si content of $x = 1.5$ (DFT) both scales are equivalent. The lines are calculated from $g(E)$ for the volume $V$ and magnetization $M$ corresponding to the measurement temperature $T_{\text{exp}}$ (circles) or $T = 0$ (DFT), respectively.

The magnetic state is connected to specific features of the electronic DOS, $D(E)$. In agreement with previous DFT results [25, 31, 33], the FM DOS in the upper panel of Fig. 3 exhibits a completely filled majority $d$-channel and a nearly half-filled minority channel. The large exchange splitting moves the mid-$d$-band minimum found in the majority channel at $-2\,\text{eV}$ right to the Fermi level $E_F$ in the minority channel, which is a stabilizing feature for the FM phase. La and Si states are essentially absent in this important energy range. In the PM phase, the original shape of the partial projected Fe-DOS is still recognizable, but it is considerably distorted through hybridization (cf. the maxima at $-3\,\text{eV}$ and $1\,\text{eV}$ in the

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FIG. 3: (Color online) Total and element-resolved electronic density of states of ferromagnetic ($M = 24.5 \mu_B/\text{f.u.}$, top) and paramagnetic ($M = 3.75 \mu_B/\text{f.u.}$, bottom) LaFe$_{11.5}$Si$_{1.5}$ from DFT. The majority spin channel is denoted by positive values, the minority channel by negative.

FIG. 4: (Color online) Element- and site-resolved difference in lattice entropy $\Delta S_{\text{lat},i} = S_{\text{lat},i}(\text{PM}) - S_{\text{lat},i}(\text{FM})$ from DFT (left side). The thick lines refer to the elemental averages, thin lines refer to values for the inequivalent lattice sites $i$. The right graph demonstrates the correlation between the site-resolved $\Delta S_{\text{lat},i}$ at $T_C$ and the change in the site-resolved minority spin DOS at $E_F$, $\Delta D_{\downarrow}^{i}(E_F) = D_{\downarrow}^{i}(E_F, \text{PM}) - D_{\downarrow}^{i}(E_F, \text{FM})$. 

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majority and minority channels, respectively) with the states of the opposite spin channel of neighboring (antiparallel) Fe. This leads to a net reduction of the moment typical for an IEM which fills the minimum at $E_F$.

The elemental decomposition of $\Delta S_{\text{lat}}$ in Fig. 4 (left) reveals that the contribution of La and Si is vanishing or slightly negative, while the anomalous increase is associated with the Fe sites. These show a large spread according to the chemical and electronic configuration, which have also a strong influence on the interatomic spacings [12, 45, 53]. Since symmetry does not change, the anomalous sign of $\Delta S_{\text{lat}}$ is thus solely related to the change of the magnetic state of Fe. States at $E_F$ are important for the screening of perturbations from a displaced atomic core. Consequently, the disappearance of minima or maxima in $D(E)$ around $E_F$ in several Fe-based materials through positional and chemical disorder has been identified as the cause of anomalous softening or stiffening, respectively [54–56]. Indeed, we can also identify a clear correlation between the changes between PM and FM phase in the site-resolved lattice entropy $\Delta S_{\text{lat},i}$ and in the partial DOS $\Delta D_i(E_F)$ of the respective site $i$. This trend is particularly pronounced for the minority electrons (Fig. 4, right) and originates from the IEM of Fe. Another consequence of the strong increase in $D(E_F)$ is a twice as large Sommerfeld constant for the electronic specific heat $\gamma_{\text{PM}} = 56.1 \text{ mJ kg}^{-1}\text{K}^{-2}$ compared to $\gamma_{\text{FM}} = 28.8 \text{ mJ kg}^{-1}\text{K}^{-2}$. Albeit $S_{\text{el}}$ appears negligibly small compared to $S_{\text{lat}}$, the substantial change in $\gamma$ causes a considerable cooperative contribution of the electronic subsystem to the phase transition (cf. Fig. 2), similar to metamagnetic $\alpha$-FeRh [57].

We conclude that the large magneto- and barocaloric effect in La-Fe-Si relates to the cooperative contributions of the interacting electronic, vibrational and magnetic subsystems to the entropy change, which arises solely from the Fe-sites. The link to the electronic scale proves that the itinerant nature of Fe-magnetism in combination with a low electronic DOS at $E_F$ in the FM phase is responsible for both, the anomalous magnetoelastic softening, which leads to a significant $\Delta S_{\text{lat}}$, and the sizeable $\Delta S_{\text{el}}$. Both favor low-volume, low-moment configurations contributing to the Invar-type (over-)compensation of thermal expansion in the FM phase and foster an early, first-order-type transformation to the magnetically disordered phase. Maximizing the Fe-content might thus be a promising strategy to improve the magnetocaloric performance of the material, but the band-filling should be adjusted by additional components.

Despite its apparent complexity, La-Fe-Si can serve well as a model system to unravel
the relevant contributions to magnetocaloric and Invar effect, which can be addressed by both, contemporary first-principles methodology and state-of-the-art scattering techniques. Since La and Si do not take part in the phase transformation, NRIXS has proven to be a suitable experimental method to determine the specific vibrational contribution to the entropy change. NRIXS could in principle be applied with external magnetic fields, providing a perspective to obtain an in situ characterization of the intrinsic lattice contributions to the magnetocaloric cycle and moment-volume-anomalies. In turn, we see the simplified 28 atom pseudo-ordered primitive cell in which we model the distribution of Si atoms and PM disorder, justified by the excellent agreement in the vibrational density of states of the Fe atoms. It provides thus a suitable basis for the computational exploration of quarternary non-stoichiometric compositions with better performance.

The authors would like to thank P. Entel (Duisburg-Essen), G. Bayreuther and J. Kirschner (Halle) and S. Fähler (Dresden) for important discussions and support. We are grateful to U. v. Hörsten (Duisburg-Essen) and Wenli Bi (Argonne) for technical assistance. Calculations were carried out on the massively parallel computers (Cray XT6/m and Opterox) of the Center of Computational Sciences and Simulation, CCSS, of the University of Duisburg-Essen. Funding by the DFG via SPP1239, SPP1599 and SPP1538 is gratefully acknowledged. BRC (RUB/UCF) was funded by the US National Science Foundation (nsf-dmr 1207065). Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357.

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