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Phonon densities of states of face-centered-cubic Ni-Fe alloys

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Inelastic neutron scattering and nuclear resonant inelastic x-ray scattering were used to determine the phonon densities of states of face-centered-cubic Ni-Fe alloys. Increasing Fe concentration results in an average softening of the phonon modes. Chemical ordering of the Ni0.72Fe0.28 alloy results in a reduction of the partial vibrational entropy of the Fe atoms but does not significantly change the partial vibrational entropy of the Ni atoms. Changes in the phonon densities of states with composition and chemical ordering are discussed and analyzed with a cluster expansion method. © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4794354]

Ni-Fe alloys are technologically important as they exhibit low coefficients of thermal expansion (Invar behavior) and are promising candidates for magnetocaloric applications.3 At elevated temperatures, these alloys are stable as random solid solutions in the face-centered-cubic (fcc) crystal structure over the entire composition range. Alloy compositions near 23 at. % Fe undergo a chemical ordering transition at 517 °C, where a low-temperature, chemically ordered L12 phase (AuCu3 prototype) transforms to the high-temperature, chemically disordered A1 phase (Cu prototype).1 Differences in vibrational entropy are thermodynamically important for order-disorder transitions especially at high temperatures.3 The vibrational entropy is calculated from the phonon density of states (DOS). In what follows, measurements of the DOS of fcc Ni-Fe alloys are described and changes with alloying and ordering are parameterized and discussed.

Alloys of Ni1−xFex with nominal compositions x = {0.05, 0.10, 0.28, 0.50, 0.60, 0.70} were prepared from foils of 99.9% purity Ni and 96.06% enriched 57Fe by arc-melting under an argon atmosphere. Electron microprobe measurements confirmed the compositions to be accurate to 0.4 at. %. The ingots were cold rolled to thicknesses between 30 and 60 μm. To remove strains and ensure a random solid solution, the foils were sealed in quartz tubes under a partial argon atmosphere, annealed for 80 min at 1000°C, and quenched into iced brine. To induce ordering in the Ni0.72Fe0.28 alloy, the sample was allowed to slow cool from 1000°C to 455°C over 40 h, then held at 455°C for 4 weeks followed by air cooling. The aging condition was in accordance with the chemical ordering study of FeNi3 by Wakelin and Yates.5

Nuclear resonant inelastic x-ray scattering (NRIXS)6–8 was performed at beamline 16-ID-D at the Advanced Photon Source, Argonne National Laboratory. The incident photon energy was tuned to 14.413 keV, the nuclear resonance energy of 57Fe. Data were collected in scans of incident photon energy from −80 to +80 meV around the resonant energy. The monochromator resolution function was measured in-situ using a single APD in the forward direction, and was found to be 2.2 meV FWHM. The NRIXS data were reduced with the software PHENIX.9 The resulting 57Fe phonon partial DOS curves are shown in Figs. 1 and 2.

Inelastic neutron scattering (INS) measurements on alloys of compositions x = {0.05, 0.28, 0.70} were performed with the wide angular-range chopper spectrometer (ARCS)10 at the Spallation Neutron Source at the Oak Ridge National Laboratory. These samples were prepared from natural Fe (i.e., with no enrichment of 57Fe) and were cold rolled to a thickness of 350 μm. The INS samples were given the same heat treatments used for the NRIXS samples. The measurements were performed with a monochromatic beam of neutrons with an incident energy of 80 meV. The instrument resolution was measured using a diamond powder with the same incident energy. The FWHM in wave-vector space was 0.06 Å−1 and in energy space was 2.5 meV. Integrating the neutron scattering intensity around the elastic peak from −5 to +5 meV provides diffraction patterns (Fig. 3). The breadth of the diffraction patterns in Fig. 3 is due to instrument resolution. Details of the data reduction procedures are described elsewhere,11–14 and the resulting neutron-weighted phonon DOS curves are shown in Figs. 1 and 2. The results are in agreement with the measurements of Hallman and Brockhous.15

Despite Fe and Ni having similar coherent scattering lengths of bFe = 9.45 × 10−15 m and bNi = 10.3 × 10−15 m, the difference is enough to clearly generate superlattice reflections in the annealed Ni0.72Fe0.28 sample (Fig. 3). An order parameter L = 0.37 was determined from the ratio of the intensities of the (100) and (110) superlattice peaks.
intensities to the (220) fundamental peak, following the method of Ziller et al.\textsuperscript{16} The intensity of the superlattice peaks for a perfectly ordered sample was calculated by setting $L = 1$ and solving for the ratio of the intensities (solid diamonds in Fig. 3).

The vibrational entropy $S_{\text{ph}}$ is obtained from the normalized phonon DOS, $g(E)$

$$S_{\text{vib}}(T) = 3k_B \int_0^\infty g(E) \left(1 + n(T)\right) \ln \left(1 + n(T)\right) - n(T) \ln(n(T)) dE,$$

where $n(T) = (\exp(E/(k_B T)) - 1)^{-1}$ is the Planck distribution for phonon occupancy.\textsuperscript{17} The partial vibrational entropy of the Fe atoms from the NRIXS measurements and the Ni atoms from a combination of the NRIXS and INS measurements is plotted in Fig. 4. The total vibrational entropy of the alloy is a concentration-weighted sum of the Ni and Fe values. As a function of concentration, the random solid solution has a nearly linear dependence, where increasing the Fe concentration increases the vibrational entropy. This indicates a general softening (shift to lower energies) of the phonon modes with Fe concentration in the fcc phase. Ordering has a large effect on the vibrational entropy of the Ni\textsubscript{97.2}Fe\textsubscript{2.8} alloy for the Fe atoms, but a negligible effect on the Ni atoms. It is generally expected that a reduction in the vibrational entropy occurs with ordering, since systems that tend to order have stronger bonds between unlike atoms. However, an exception to this trend was recently observed for V-Fe alloys.\textsuperscript{18}

Chemical ordering from the disordered alloy to the L\textsubscript{12} phase results in a larger change for the local chemical environment of the Fe atoms than for the Ni atoms. In a

![FIG. 1. $^{57}$Fe partial DOS curves from NRIXS spectra (lines with error bars) and INS DOS curves (solid circles) at 300 K for the random solid solutions. Curves are offset by multiples of 0.03 meV\textsuperscript{-1}.

FIG. 2. $^{57}$Fe partial DOS curves from NRIXS spectra (top panel) and INS DOS curves (bottom panel) at 300 K for the random solid solution and L\textsubscript{12} ordered alloy (curves with no offset). For comparison (curves offset by 0.03 meV\textsuperscript{-1}), the disordered Ni\textsubscript{0.72}Fe\textsubscript{0.28} alloy is compared to the $^{57}$Fe DOS of Ni\textsubscript{0.95}Fe\textsubscript{0.05} (top panel) and the DOS of Ni from INS (bottom panel).

![FIG. 3. Scattering as a function of momentum transfer $Q$ from neutron scattering for disordered (dashed line) and ordered (solid line) Ni\textsubscript{0.72}Fe\textsubscript{0.28}. Superlattice reflections indicative of chemical ordering are denoted with an “s.” The diamond shows the calculated intensity of the (100) and (110) superlattice reflections for complete ordering.

![FIG. 4. Phonon entropy at 300 K of NiFe alloys as a function of composition.](image)
disordered alloy, the average number of Ni atoms in the first-nearest-neighbor shell (1nn) of an Fe atom is $(1 - x) \times 12$, which is 8.64 for $x = 0.28$. Perfect chemical ordering results in a complete 1nn shell of Ni atoms for the Fe atom at Ni$_3$Fe stoichiometry. Off-stoichiometry, and for different degrees of short- and long-range chemical ordering, there is an increase in the number of Ni atoms in the 1nn shell of Fe with increasing chemical order. For the Ni atoms, the number of Fe atoms in the 1nn shell does not change as much with chemical ordering (from three 1nn Fe atoms for the chemically disordered Ni$_{0.73}$Fe$_{0.25}$ to four 1nn Fe atoms for the L1$_2$ ordered Ni$_3$Fe). Variations in chemical composition, and variations in short- and long-range order, alter the number of Ni atoms in the 1nn shell of Fe atoms.

Chemical ordering results in a change in the number of 1nn Ni atoms for Fe atoms that is similar to a reduction in Fe concentration. Figure 2 shows a comparison of the disordered Ni$_{0.72}$Fe$_{0.28}$ with the ordered alloy and the disordered Ni$_{0.95}$Fe$_{0.05}$. For the low-energy modes below 30 meV, the effect on the DOS with ordering is similar to reducing the Fe concentration. However, at higher energies, there is a shift to higher frequencies with decreasing Fe concentration and no change upon ordering.

A useful way to parameterize the effect of chemical ordering on the DOS is to use the cluster expansion formalism. Details of the methodology can be found elsewhere. Here, a least-squares inversion was performed using the DOS of the random solid solutions from NRIXS using 3 terms in the expansion, giving the interaction DOS (IDOS) curves of Fig. 5. The IDOS functions have physical meaning from the type of cluster they represent. The $n = 0$ term corresponds to the empty lattice and its IDOS is the Ni$_{0.50}$Fe$_{0.50}$ random solid solution. The $n = 1$ term corresponds to the point cluster, and gives the concentration dependence of the DOS. The $n = 2$ term corresponds to the pair cluster and gives the pairwise dependence of the DOS. The interesting aspect of the curves in Fig. 5 is that the pair term is similar in shape but larger in magnitude than the point term. This indicates that chemical ordering has a larger effect on the DOS than changes in concentration, although the two affect the DOS in similar ways. Figure 4 shows that the effects of chemical ordering are comparable to those of composition, even though the change in chemical order was relatively small in our samples.

To summarize, phonon spectra were measured for fcc Ni-Fe alloys using inelastic x-ray and neutron scattering techniques. Chemical ordering was observed from the neutron scattering measurements, which resulted in a decrease in the vibrational entropy and a change in the phonon density of states of the Fe atoms that was similar to the changes induced by alloying. This chemical dependence of the Fe atom DOS was confirmed using the cluster inversion method, showing a relatively strong dependence on the state of chemical order. In contrast, the Ni atom vibrations did not show a large change with chemical ordering, which may be attributed to the smaller change in the local chemical environment as compared to the Fe atoms.

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