

# Supplemental Material for “The temperature dependence of phonons in Pd<sub>3</sub>Fe through the Curie temperature”

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## I. SAMPLE PREPARATION

### A. Conventional X-Ray Diffraction

Characterization was performed on the Pd<sub>3</sub><sup>57</sup>Fe sample with x-ray diffractometry using Cu K $\alpha$  radiation. The diffraction measurements were performed on the sample after the heat treatment described in the main text and after the nuclear resonant inelastic x-ray scattering (NRIXS) measurements at high temperature, with results shown in Fig. 1.

The diffraction patterns include fundamental peaks expected from fcc and fcc-based structures. The patterns also include superlattice peaks expected in the  $L1_2$  structure, including (110), (210), (211), (320), and (321). The presence of these peaks are indicative of long-range  $L1_2$  chemical order in the sample before and after the NRIXS measurements. X-ray diffractometry showed that the chemical order was at least as high after the NRIXS measurements as before.

The lattice parameter of Pd<sub>3</sub>Fe was measured to be  $3.852 \pm 0.001 \text{ \AA}$ . All diffraction measurements provided similar values of lattice parameters within the margin of error.

### B. Mössbauer Spectrometry

Mössbauer spectra were collected from conversion electrons in backscatter geometry using a constant acceleration spectrometer with a <sup>57</sup>Co in Rh  $\gamma$ -ray source. Velocity and isomer shift calibrations were performed by reference to room temperature  $\alpha$ -iron. The conversion electron Mössbauer spectra of the Pd<sub>3</sub><sup>57</sup>Fe foil sample over the course of this experiment are shown in Fig. 2.

The hyperfine field was measured from Mössbauer spectrometry for the previously annealed Pd<sub>3</sub><sup>57</sup>Fe sample before the second heat treatment described in the main text (“Ordered-I”), after this heat treatment (“Ordered-II”), and after the high-temperature NRIXS measurements. These values are reported in Table I, together with the hyperfine field of the ordered Pd<sub>3</sub>Fe and disordered Pd<sub>0.73</sub>Fe<sub>0.27</sub> samples measured by Longworth [1].

From the mean hyperfine fields, it appears that there was little change in the state of chemical order near the surface of the sample probed by the conversion electron Mössbauer spectrometer.

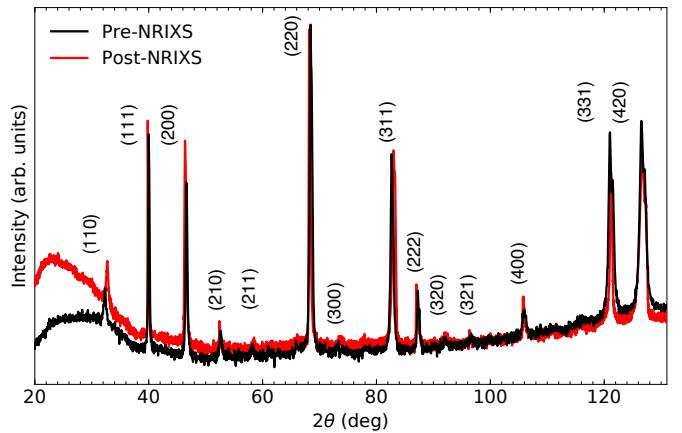


FIG. 1. X-ray diffraction patterns of Pd<sub>3</sub><sup>57</sup>Fe (“Ordered-II”) collected on a Cu K $\alpha$  laboratory diffractometer. Measurements were performed on the sample after the heat treatment (“Pre-NRIXS”) and after the NRIXS measurements (“Post-NRIXS”). The labeled peaks include both fundamental and superlattice peaks. The intensity is displayed in a logarithmic scale.

TABLE I. Hyperfine fields  $H$  and change in the hyperfine field  $\Delta H$  in the Pd<sub>3</sub><sup>57</sup>Fe sample at different stages of this study, shown together with measurements performed by Longworth [1]. For the Pd<sub>3</sub><sup>57</sup>Fe sample, the hyperfine field for “Ordered-II” is treated as a reference for  $\Delta H$ . For the measurements performed by Longworth, the hyperfine field for the ordered sample is treated as a reference for  $\Delta H$ .

Sample	Hyperfine Field $H$ (kOe)	$\Delta H$ (kOe)
Ordered-I	$286.402 \pm 0.01$	-5.849
Ordered-II	$292.251 \pm 0.01$	0
Post-NRIXS	$290.821 \pm 0.01$	-1.430
Ordered (Longworth)	$285.5 \pm 1$	0
Disordered (Longworth)	$278 \pm 1$	-7.5

## II. SYNCHROTRON MEASUREMENTS

### A. Synchrotron X-ray Diffraction

In situ synchrotron x-ray diffraction (XRD) measurements were performed at beamline 16ID-D of the Advanced Photon Source at Argonne National Laboratory using a monochromatic beam at 14.413 keV and a resistive heating furnace with a kapton window for x-ray transmission. Diffraction was measured using a Mar

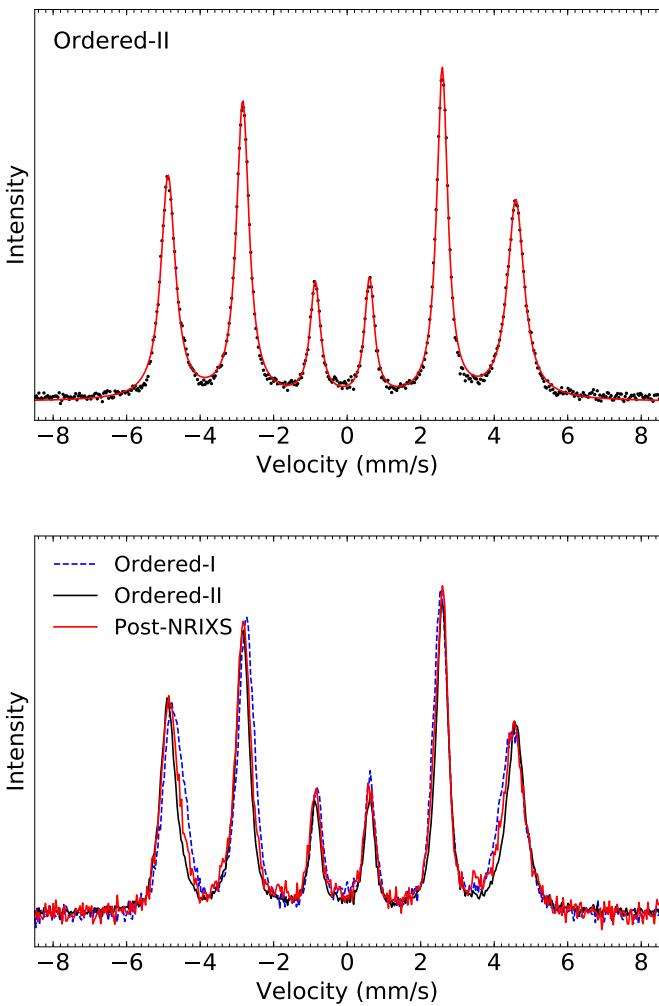


FIG. 2. (Top) Room temperature Mössbauer spectrum of the annealed  $\text{Pd}^{57}\text{Fe}$  foil sample before the NRIXS experiment (Ordered-II). (Bottom)  $\text{Pd}^{57}\text{Fe}$  Mössbauer spectra for the “Ordered-I” state, “Ordered-II” state, and after the NRIXS experiment.

CCD detector plate. The two-dimensional diffraction rings on the image plate (Fig. 3(a) and (b)) were integrated with the FIT2D [2] program to produce diffraction patterns of intensity vs.  $2\theta$  (Fig. 3(c)).

For measurements above the Curie temperature, a 16 micron-thick piece of aluminum foil was placed over the kapton window to reflect the radiative heat from the furnace away from the avalanche photodiodes used in the NRIXS measurements. The aluminum foil caused the additional diffraction rings at 627 and 786 K. These ex-

traneous rings were masked in the FIT2D program, resulting in the dips in intensity in the integrated diffraction patterns for 627 and 786 K.

The lattice parameters of the  $L1_2$ -ordered  $\text{Pd}_3\text{Fe}$  were determined from synchrotron XRD to be 3.8541 Å at 298 K; 3.8546 Å at 417 K; 3.8636 Å at 459 K; 3.8661 Å at 485 K; 3.8719 Å at 627 K; 3.8854 Å at 786 K.

These results are consistent with a prior XRD measurement of the lattice parameter of  $\text{Pd}_3\text{Fe}$  with respect to temperature [3].

## B. Nuclear Resonant Inelastic X-ray Scattering

NRIXS measurements were performed on  $\text{Pd}_3^{57}\text{Fe}$  at seven temperatures from 298 to 786 K at beamline 16ID-D of the Advanced Photon Source at Argonne National Laboratory. For each temperature, the NRIXS spectrum was measured by scanning the energy transfer from  $-80$  to  $+80$  meV around the resonant energy of  $^{57}\text{Fe}$  in several scans that were combined for final analysis. The spectra are shown in Fig. 4. The energy resolution of all NRIXS measurements was measured to be 2.2 meV (FWHM) at the elastic line. The instrument resolution function is also shown in Fig. 4.

The PHOENIX software package was used to extract the  $^{57}\text{Fe}$  partial phonon densities of states (pDOS) from the NRIXS spectra [4]. The data reduction procedure in the PHOENIX software package involves the removal of the resonant elastic peak and the multi-phonon processes from the NRIXS spectra. The one-, two-, and three-phonon contributions to the NRIXS spectra at 298 and 786 K are shown in Fig. 5.

Other physical quantities were calculated from the data reduction procedure in PHOENIX. One such physical quantity is the Lamb-Mössbauer factor, plotted in Fig. 6. The Lamb-Mössbauer factor was also calculated from fits to the nuclear forward scattering (NFS) spectra with the CONUSS software package [5]. Due to the low counts in the nuclear forward scattering spectra, the Lamb-Mössbauer factors obtained from the NFS spectra are expected to have a greater error than those obtained from the data reduction of the NRIXS spectra.

Figure 7 shows previous room temperature NRIXS measurements of the  $L1_2$ -ordered  $\text{Pd}^{57}\text{Fe}$  compound in its “Ordered-I” state and the disordered fcc alloy  $\text{Pd}_{0.75}^{57}\text{Fe}_{0.25}$ . The  $^{57}\text{Fe}$  pDOS for the disordered sample is considerably different from the “Ordered-I” pDOS and the pDOS from this study (“Ordered-II”).

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<sup>3</sup> J. Jääskeläinen and E. Suoninen, Phys. Status Solidi A **63**, 241 (1981).

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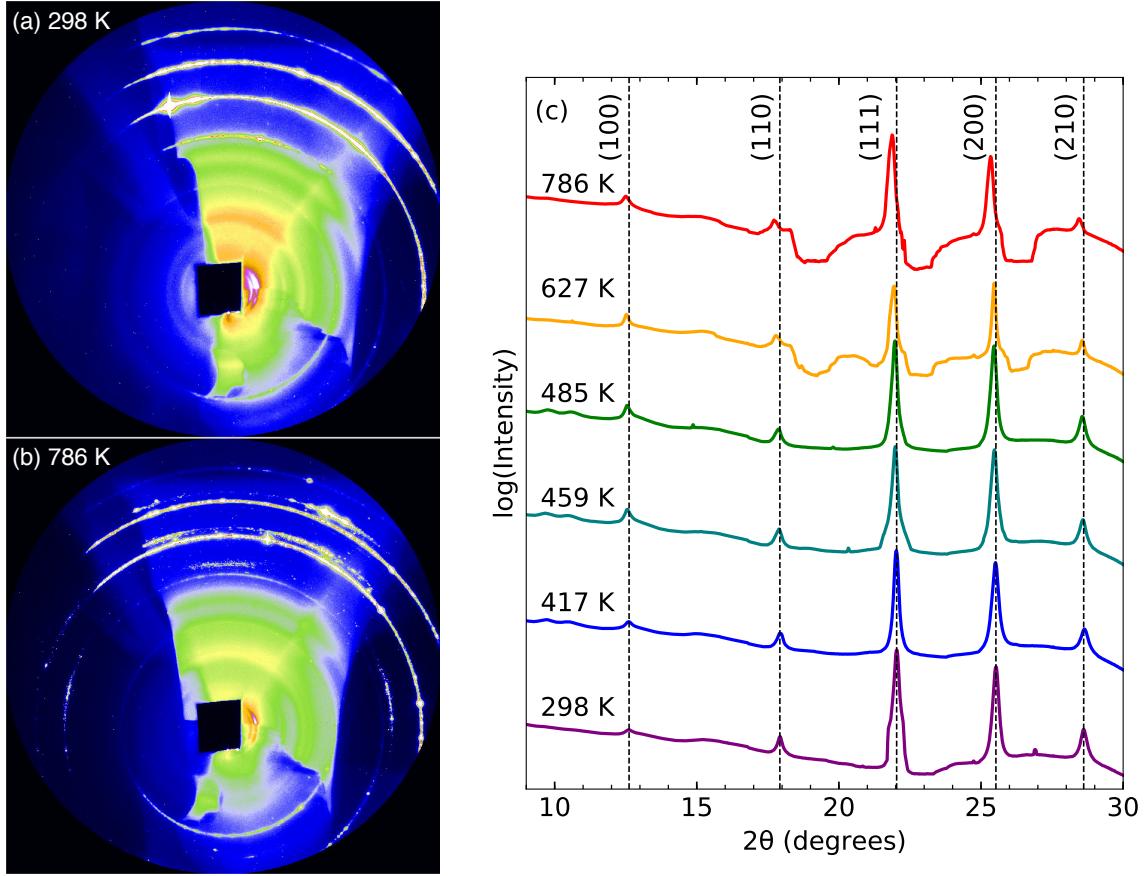


FIG. 3. Two-dimensional synchrotron diffraction patterns of Pd<sub>3</sub>Fe recorded on a CCD detector plate at (a) 298 K and (b) 786 K. (c) One-dimensional synchrotron x-ray diffraction patterns of Pd<sub>3</sub><sup>57</sup>Fe from 298 to 786 K. The black dashed lines are the locations of the 298 K diffraction peaks. The dips in intensity for 627 and 786 K are where extraneous diffraction peaks from the aluminum foil were masked.

TABLE II. Physical quantities calculated from the integration of the <sup>57</sup>Fe phonon DOS: The Fe partial vibrational heat capacity, the vibrational kinetic energy, and the mean force constant.

Temperature (K)	Fe Partial Heat Capacity (k <sub>B</sub> /atom)	Kinetic Energy (meV/atom)	Mean Force Constant (N/m)
298	2.8382 ± 0.0106	13.5647 ± 0.0603	2.435 ± 0.024
417	2.8355 ± 0.0376	19.8122 ± 0.4101	2.440 ± 0.030
459	2.9227 ± 0.0535	20.6811 ± 0.5960	2.421 ± 0.027
485	2.8686 ± 0.0385	22.0571 ± 0.4264	2.448 ± 0.043
535	2.9125 ± 0.0518	23.7510 ± 0.5040	2.360 ± 0.034
627	2.9702 ± 0.0408	28.4609 ± 0.4977	2.343 ± 0.040
786	3.0107 ± 0.0434	33.1471 ± 0.5778	2.340 ± 0.047

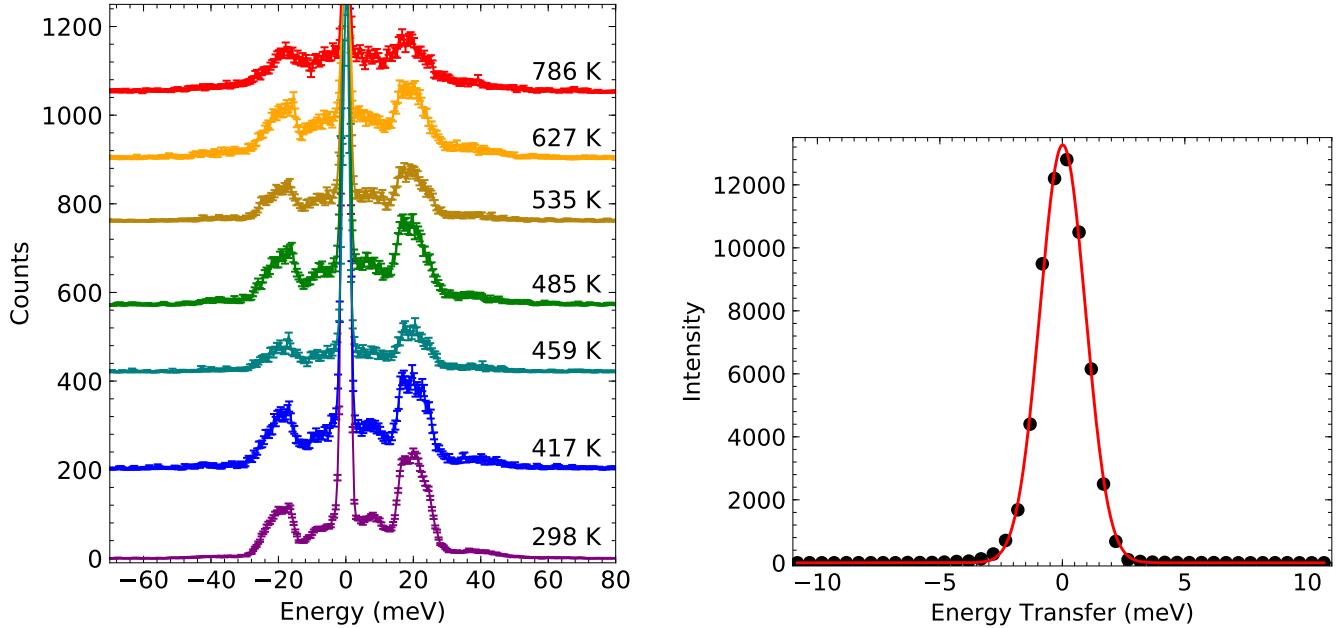


FIG. 4. (Left) Raw NRIXS scattering spectra showing  $^{57}\text{Fe}$  vibrational excitations in  $\text{Pd}_3^{57}\text{Fe}$  as a function of scattering energy. Spectra are collected over a range of temperatures. (Right) The elastic line of the raw scattering spectrum of  $^{57}\text{Fe}$  at room temperature, used as the instrument resolution function for the NRIXS measurements.

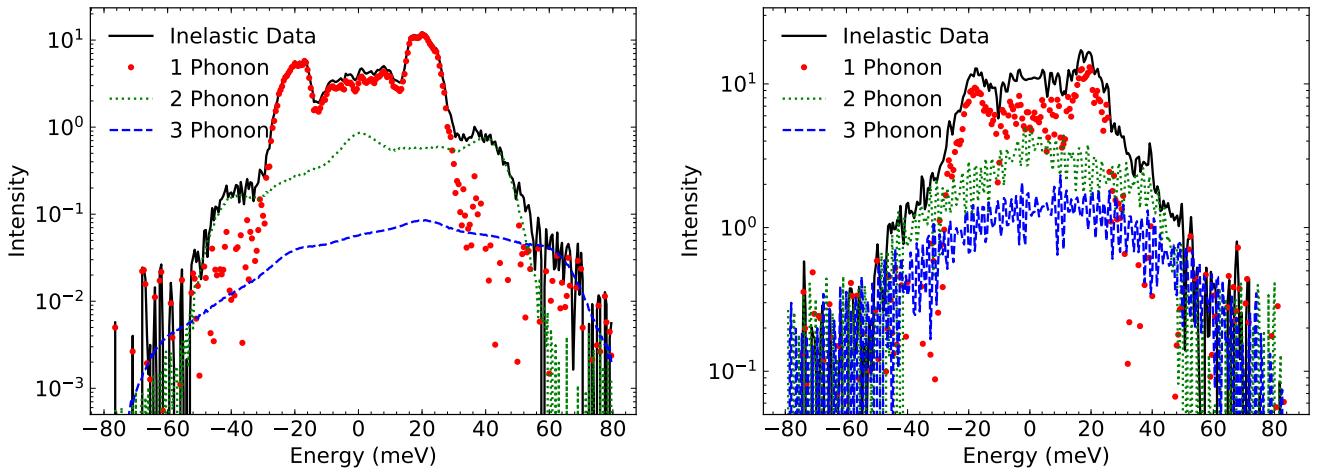


FIG. 5. The multi-phonon components of the NRIXS spectra of  $\text{Pd}_3^{57}\text{Fe}$  at (left) 298 K and (right) 786 K.

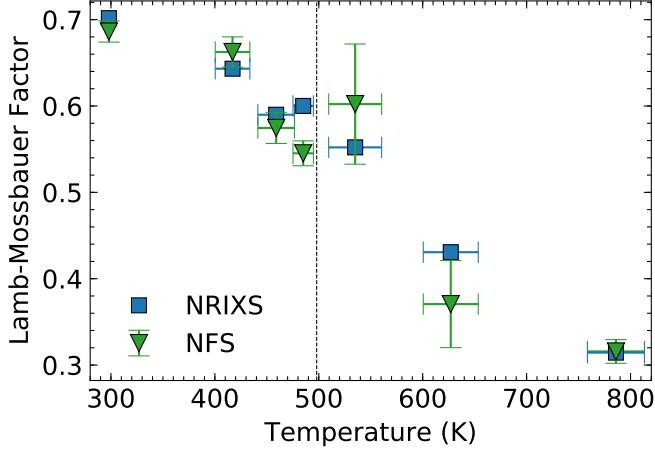


FIG. 6. Lamb-Mössbauer factors obtained from NRIXS (blue squares) and NFS (green triangles).

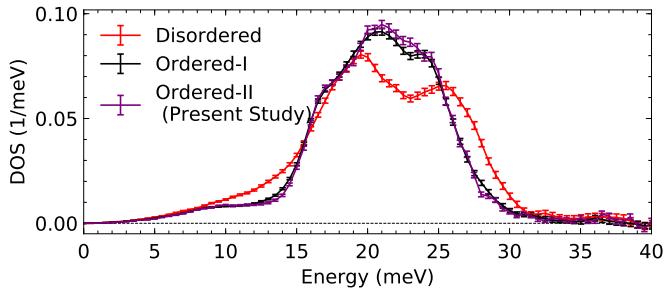


FIG. 7. The room temperature  $^{57}\text{Fe}$  pDOS of the  $\text{Pd}_3^{57}\text{Fe}$  sample measured in this study (purple) compared with prior measurements of the room temperature  $^{57}\text{Fe}$  pDOS of ordered  $\text{Pd}_3^{57}\text{Fe}$  (black) and the disordered fcc alloy  $\text{Pd}_{0.75}^{57}\text{Fe}_{0.25}$  (red).