Supplementary Material for:
Nonharmonic contributions to the high-temperature phonon thermodynamics of Cr

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I. MULTIPLE SCATTERING

The experiment was designed to minimize the effects of multiple scattering. This was achieved by choosing a sufficiently thin sample of Cr. The ratio of double (multiple) scattering to single scattering is

\[ 1/2 \left( t/\tau \right), \]

where $t$ is the sample thickness and $\tau$ is the characteristic scattering length of

\[ \tau = 1/(\rho \sigma). \]

Here $\sigma = 3.5$ barns for the total scattering of a Cr nucleus and $\rho = 8.3 \times 10^{22}$ nuclei/cm$^3$. For the Cr pieces in this experiment, which were ~0.15 cm thick, the ratio of single to double scattering is 0.022, or 2%. Despite some directions in the sample where the neutron paths were longer, the sample is still thin enough to neglect multiple scattering.

II. AB INITIO MODELING

A. Quasi-harmonic

Phonon calculations with the quasi-harmonic (QH) approximation used the Phonopy package [1]. The finite difference method was used to generate forces on atoms. Force constant matrices were constructed and transformed into the dynamical matrix,

\[ D(\mathbf{q}) e_{qs} = \omega_{qs}^2 e_{qs}, \]

where $D(\mathbf{q})$ is the dynamical matrix, $\mathbf{q}$ is the phonon wave vector, $s$ is the phonon band index, $\omega_{qs}$ and $e_{qs}$ are the frequency and polarization vector of the phonon mode with $\mathbf{q}$, $s$. With all $\{ \omega_{qs} \}$, the vibrational contribution to the free energy is

\[ F_{\text{vib}} = \frac{1}{2} \sum_{qs} \hbar \omega_{qs} + k_B T \sum_{qs} \ln \left[ 1 - \exp \left( -\hbar \omega_{qs} / k_B T \right) \right]. \]

Temperatures from 0-1500 K were considered using a grid of 0 K supercells scaled in volume by ±0.5%, ±1%, ±1.5%. The Helmholtz free energy for each volume was calculated and minimized at different temperatures using the Birch-Murnaghan equation of state. Minima of the fitted free energy curves gave the QH volumes at the temperatures of interest. Quasi-harmonic phonon properties were calculated with these volumes. The calculated phonon density of states was convoluted with a Gaussian of 1.0 meV to approximate the broadening due to instrumental resolution.

B. Anharmonic

Phonon calculations with the anharmonic (AH) approximation used the stochastic Temperature Dependent Effective Potential Method (sTDEP) [2]. Supercells with displaced atoms were created by stochastic sampling. For a cell of $N_o$ atoms with mass $m_i$, the atomic positions, $\{u_i\}$, were created using a harmonic normal-mode transformation,

\[ u_i = \sum_{s=1}^{3N_o} e_{is} \langle A_{is} \rangle \sqrt{-2 \ln \xi_1 \sin (2 \pi \xi_2)}, \]

where $\xi_n$ are uniformly distributed numbers between 0 and 1 (the Box-Muller transform). The thermal amplitude, $\langle A_{is} \rangle$, of normal mode $s$ with eigenvector $e_{is}$ is

\[ \langle A_{is} \rangle = \frac{1}{\omega_s} \sqrt{\frac{\hbar \omega_s(n_s + \frac{1}{2})}{m_i}} \approx \frac{1}{\omega_s} \sqrt{\frac{k_B T}{m_i}}, \]

where $n_s = \left( e^{\hbar \omega_s / k_B T} - 1 \right)^{-1}$ is the thermal occupation of phonon mode $s$ and $\hbar \omega \ll k_B T$ denotes the classical limit at high temperatures.

Energies and forces from calculations of an ensemble of supercells with thermally displaced atoms were obtained with a least squares fit to a model Hamiltonian.
A grid of four temperatures, \{0, 330, 1000, 1500\} K, and nine volumes was created. For each volume-temperature point, ten thermally displaced supercells were stochastically generated using force constants from a model pair potential. Static calculations were performed on each supercell to obtain energy-force-displacement data. Quadratic and cubic force constants were re-generated for each temperature using these data sets. The free energy surface,

\[ F(V, T) = U_0(V, T) + F_{\text{vib}}(V, T), \]

for each volume-temperature point was calculated using sTDEP. The baseline, \(U_0(V, T)\), and the free energy from lattice vibrations,

\[ F_{\text{vib}} = \int_0^\infty g(\omega) \left\{ k_B T \ln \left[ 1 - e^{-\frac{\omega}{k_B T}} \right] + \frac{\hbar \omega}{2} \right\} d\omega, \]

depend explicitly on volume and temperature. These free energies were fit to the Birch-Murnaghan equation of state to find the optimized volume for a given temperature.

The phonon DOS,

\[ g(\omega) = \sum_s \delta(\omega - \omega_s), \]

also depends explicitly on volume and temperature. Linewidths are obtained from the imaginary component,

\[ \Gamma_s(\Omega) = \frac{\hbar \pi}{16} \sum_{s's''} |\Phi_{s's''}|^2 \]

\[ \times \left\{ (n_{s'} + n_{s''} + 1) \delta(\Omega - \omega_{s'} - \omega_{s''}) + (n_{s'} - n_{s''}) \right. \]

\[ \left. \times \delta(\Omega - \omega_{s'} + \omega_{s''}) - \delta(\Omega + \omega_s - \omega_{s''}) \right\}. \]

This sum is taken over all possible three-phonon interactions, where \(\Phi_{s's''}\) is the three-phonon matrix element obtained from the cubic force constants.

A Kramers-Kronig transformation was used to get the frequency shifts,

\[ \Delta(\Omega) = \frac{1}{\pi} \int \frac{\Gamma(\omega)}{(\omega - \Omega)} d\omega. \]

As shown in Eq. 10, these shifts are the real part of the phonon self-energy.

Anharmonic phonon densities of states curves were calculated using the real and imaginary parts of the phonon self-energy,

\[ g_{\text{anh}}(\omega) = \sum_s \left\{ \frac{2\omega_s \Gamma_s(\omega)}{[\omega^2 - \omega_s^2 - 2\omega_s \Delta_s(\omega)]^2 + 4\omega_s^2 \Gamma_s^2(\omega)} \right\}. \]

In the limit where \(\Delta, \Gamma \rightarrow 0\) Eq. 13 reduces to Eq. 9.

### III. BORN-VON KÁRMÁN MODELING

The Born-von Kármán formalism relates interatomic force constants of crystalline solids to phonon frequencies. To solve for phonon frequencies, the interatomic interactions in the dynamical matrix are truncated to the first few nearest-neighbor interactions. Below is a description of how the force constants are extracted from the DOS of body-centered cubic (bcc) Cr using a genetic algorithm to obtain temperature-dependent tensorial and radial force constants [3].

#### A. Genetic algorithm

A genetic algorithm optimization was performed to obtain interatomic force constants from experimental phonon DOS employing the open-source package mystic [4]. To begin, the algorithm was used to generate many candidate solutions called a population. Each population consisted of a potential set of force constants that was randomly generated within a set of reasonable force constant bounds, where

\[ K_{1NN} = \begin{pmatrix} 1XX & 1XY & 1XY \\ 1XY & 1XX & 1XY \\ 1XY & 1XY & 1XX \end{pmatrix}, \]

\[ K_{2NN} = \begin{pmatrix} 2XX & 0 & 0 \\ 0 & 2YY & 0 \\ 0 & 0 & 2YY \end{pmatrix} \]

are the first and second nearest-neighbor tensorial force constant matrices. The dynamical matrix was constructed from each population (set of force constants) and used to generate a DOS. These DOS are compared with the experimental DOS, and solutions that best reproduce the experimental DOS (by minimizing the mean squared error) are selected as the parents of the next generation. The parent solutions seeded the next population of potential force constants by selecting random combinations of parent parameters and also introducing random changes, or mutations. Least squares fitting and comparison to experiments were repeated until the population converged on a set of force constants that provided the best fit to the experimental density of states (Fig. 1). Throughout this process, solutions that generated negative frequencies were discarded due to their implication of dynamical instability in the lattice. Fully optimized force constants were then used to generate phonon dispersions with \(q\)-space resolved information.
FIG. 1. TOF INS phonon density of states and the BvK DOS from a second nearest-neighbor fit for 333, 993, and 1493 K. The BvK fit was convoluted with the instrument resolution function.

B. Tensorial and radial force constants

Tensorial force constants from the genetic algorithm optimization, previous experiments, and computations are presented in Table I. To visualize the effects of temperature on nearest-neighbor interactions, each matrix \((K_{1NN}, K_{2NN})\) was projected onto their respective bond directions (Fig. 2). Longitudinal and average transverse force constants are obtained, which describe the forces parallel and perpendicular to the bond direction. The longitudinal force constants are significantly higher than the average transverse force constants. Second nearest-neighbor longitudinal force constants dominate over the first nearest-neighbors, but both show a large decrease with an increase in temperature, as generally expected. The second nearest-neighbor transverse force constants remain relatively constant with temperature, while the first nearest-neighbor average transverse force constants exhibit an unusual temperature dependence.

The radial force constants from the BvK analysis, sTDEP, the QH approximation, and previous experiments are shown in Fig. 2. There is good agreement between our TOF INS experiments, previous measurements, and sTDEP calculations. QH calculations predict the nearest neighbor longitudinal force constants to be much lower than the other methods. This approximation also overestimates the values for the nearest-neighbor transverse force constants. The inability of the QH approximation to capture the values of the 1NN force constants originates from its drastic underestimation of the \(\phi_{1xy}\) tensorial matrix component (see Table I).

IV. NEUTRON SIMULATIONS WITH MCVINE

The MCViNE (Monte-Carlo Virtual Neutron Experiment) software package was used to simulate neutron scattering from a chromium plate measured on the wide Angular-Range Chopper Spectrometer (ARCS) instrument at room temperature and above. MCViNE is a neutron ray-tracing simulation package that tracks the pathway of neutrons through the interaction with instrument optical components, scattering from the sample, interception by the detectors, and reduction to an experimentally equivalent format [7]. The sample was described with a “composite neutron scatterer,” which consisted of five rectangular slabs: the Cr sample plate, two thin Nb foils in front and behind the sample plate, and the absorbing BN frame to the left and right of the sample plate. An additional composite neutron scatterer was placed around the sample to simulate scattering from the MICAS furnace and between the sample and furnace. The design and testing of this furnace composite is described elsewhere [8].

The chromium sample is modeled with dimensions matching the sample used in the ARCS experiment and
TABLE I. Tensorial force constants from previous experiments [5, 6] and computation. Non-labeled force constants correspond to current measurements, and those labeled a, b, are Phonopy and sTDEP calculations, respectively.

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>(\Phi_{1xx})</th>
<th>(\Phi_{1xy})</th>
<th>(\Phi_{2xx})</th>
<th>(\Phi_{2yy})</th>
</tr>
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<tbody>
<tr>
<td>293[5]</td>
<td>14.35</td>
<td>6.93</td>
<td>37.70</td>
<td>-0.77</td>
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<tr>
<td>334</td>
<td>11.53</td>
<td>8.12</td>
<td>42.78</td>
<td>1.62</td>
</tr>
<tr>
<td>493</td>
<td>11.39</td>
<td>8.19</td>
<td>40.28</td>
<td>2.41</td>
</tr>
<tr>
<td>592</td>
<td>11.42</td>
<td>8.24</td>
<td>38.62</td>
<td>2.12</td>
</tr>
<tr>
<td>693</td>
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<td>37.38</td>
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<tr>
<td>894</td>
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</tr>
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<td>12.661</td>
<td>-0.823</td>
<td>42.124</td>
<td>-4.108</td>
</tr>
</tbody>
</table>

This simulated process revealed the effect of the sample curvature on the \(S(Q, E)\) experimental inelastic spectra. The simulation allows for contributions from multi-phonon scattering and multiple scattering to be turned on or off, allowing isolation of contributions to the \(S(Q, E)\) from these effects. After reduction of experimental \(S(Q, E)\) to a phonon DOS, an unexpected intensity is observed above the phonon cutoff near 40-45 meV. Based on comparison to the phonon DOS obtained from the simulated plate, this feature is attributed to scattering resulting from the sample curvature. A 2D correction matrix was calculated from the simulated data and applied to the experimental data across the full temperature range. This correction had the effect of eliminating the unexpected intensity above the phonon cutoff.