Vibrational entropy and microstructural effects on the thermodynamics of partially disordered and ordered Ni$_3$V

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Samples of Ni$_3$V were prepared with two microstructures: (1) with equilibrium D0$_{22}$ order, and (2) with partial disorder (having a large D0$_{22}$ chemical order parameter, but without the tetragonality of the unit cell). For both materials, we measured the difference in their heat capacities from 60 to 325 K, inelastic neutron-scattering spectra at four values of $Q$ at 11 and at 300 K, and Young’s moduli and coefficients of thermal expansion. The difference in heat capacity at low temperatures was consistent with a harmonic model using the phonon density of states (DOS) curves determined from the inelastic neutron-scattering spectra. In contrast, at temperatures greater than 160 K the difference in heat capacity did not approach zero, as expected of harmonic behavior. The temperature dependence of the phonon DOS can be used to approximately account for the anharmonic contributions to the differential heat capacity. We also argue that some of the anharmonic behavior should originate with a microstructural contribution to the heat capacity involving anisotropic thermal contractions of the D0$_{22}$ structure. We estimate the difference in vibrational entropy between partially disordered and ordered Ni$_3$V to be $S_{\text{vib}}^{\text{dis}} - S_{\text{vib}}^{\text{ord}} = (0.038 \pm 0.015)k_B/\text{atom}$ at 300 K. [S0163-1829(96)02945-1]

I. INTRODUCTION

There is a growing awareness that vibrational entropy $S_{\text{vib}}$ can have a significant effect on the thermodynamic stabilities of alloy phases. Vibrational entropy has received sporadic interest over many years.$^{1-6}$ Only recently, however, have studies been performed to measure$^7-12$ or calculate accurately$^{13-16}$ the difference in vibrational entropy, $\Delta S_{\text{vib}}^{\beta-\alpha}(T)$, between two states, $\alpha$ and $\beta$, of a material. Reported values of $\Delta S_{\text{vib}}^{\beta-\alpha}$ have been in the range of 0.1–0.2 kJ/atom. Such differences in vibrational entropy are large enough to have a considerable influence on critical temperatures,$^{16}$ or the shapes of phase boundaries.$^{11}$

The direct way to determine differences in entropy at constant pressure is to measure differences in heat capacity of two states of a material over a range of temperatures, $\Delta C_p(T) = C_p^{\beta} - C_p^{\alpha}$. This can be done by differential calorimetry, and then calculating:

$$\Delta S_{\text{vib}}^{\beta-\alpha}(T) = \int_0^T \frac{\Delta C_p(T')}{T'} \, dT'.$$

(1)

If the two states of the material remain constant during the measurements, calorimetric methods using Eq. (1) are a good way to obtain $\Delta S_{\text{vib}}^{\beta-\alpha}(T)$. Fortunately, the integrand $\Delta C_p(T)/T$ is often largest at low temperatures where there is no significant atomic diffusion, so there are no changes in atomic configurations during the measurements. In the present work we used differential scanning calorimetry to measure $\Delta C_p(T)$ for two states of the metallic alloy Ni$_3$V. The material was quenched from high temperature to provide a state of partial disorder, which we confirmed to have strong chemical order, but none of the tetragonality of the equilibrium D0$_{22}$ structure.$^{17,18}$ The second state of the material was the D0$_{22}$ equilibrium structure, obtained by annealing the alloy.

The difference in the phonon density of states of the two materials, $g^{\beta}(\varepsilon) - g^{\alpha}(\varepsilon)$, where $\varepsilon$ is the phonon energy, is often the physical origin for differences in $\Delta C_p(T)$. The phonon density of states (DOS) of a material can sometimes be measured by inelastic neutron scattering. For transition-metal aluminides, it was found that the development of optical modes at high energies, associated with vibrations of the Al sublattice in the ordered structure, was the change in the phonon DOS most important to the vibrational entropy.$^9,10$ It was also found, however, that interpreting phonon dispersion curves from single crystals of chemically disordered alloys runs the risk of underestimating the density of high-frequency modes.$^{10}$ In the present work we attempted to measure the phonon DOS by a more direct inelastic neutron-scattering experiment on polycrystalline samples. We recorded energy-loss spectra at various values of momentum transfer, $Q$, to measure incoherent inelastic scattering and coherent inelastic scattering. The alloy Ni$_3$V proved convenient for this study, since the incoherent scattering cross sections of Ni and V are nearly identical, and the lattice dynamics of fcc Ni are well known. We obtained approximate phonon DOS curves from inelastic neutron-scattering spectra measured at 11 and 300 K. The phonon DOS curves accounted for the low-temperature part of the $\Delta C_p(T)$ measured by calorimetry.

The temperature dependence of the phonon DOS curves could account for much of the anharmonic part of $\Delta C_p(T)$ measured at temperatures greater than 160 K. Using measured values for thermal expansion and elastic moduli, however, we found a discrepancy in the anharmonic contribution calculated as the classical difference, $C_p - C_V$. We
argue that this discrepancy could originate with a microstructural mechanism for storage of elastic energy. The difference in vibrational entropy of the partially disordered and ordered Ni$_3$V was estimated to be $S^\text{ph}_{\text{dis}}-S^\text{ph}_{\text{ord}}=+(0.038 \pm 0.015)k_B/\text{atom}$ at 300 K.

### II. PHONON DOS AND HEAT CAPACITY

We calculate the heat capacity at constant pressure $C_p(T)$ as follows. The phonon energy in the lattice $E_{\text{ph}}$ is

$$E_{\text{ph}} = \int_0^\infty g(\epsilon)\epsilon\left(\frac{1}{2} + \frac{1}{e^{\epsilon/kT}-1}\right) d\epsilon. \hspace{1cm} (2)$$

The temperature dependence of $E_{\text{ph}}$ occurs through both the change in the phonon occupancy factor of each mode, and the change in the phonon energies:

$$\frac{\partial E_{\text{ph}}}{\partial T} = 3 \int_0^\infty g_T(\epsilon)\frac{\epsilon^2 e^{\epsilon/kT}}{kT^2 (e^{\epsilon/kT}-1)^2} d\epsilon + 3 \int_0^\infty g_T(\epsilon)\frac{\epsilon}{kT} \frac{1}{2} e^{\epsilon/kT} d\epsilon, \hspace{1cm} (3)$$

where $g_T(\epsilon)$ is the phonon DOS at $T=0$. We recognize the first term in Eq. (3) as the heat capacity at constant volume, $C_V(T)$:

$$C_V(T) = 3 \int_0^\infty g_T(\epsilon)\frac{\epsilon^2 e^{\epsilon/kT}}{kT^2 (e^{\epsilon/kT}-1)^2} d\epsilon, \hspace{1cm} (4)$$

which is equal to $C_p(T)$ when the phonon frequencies are unchanged with temperature so that $\partial \epsilon/\partial T=0$. In what follows, we assume that the individual phonon frequencies undergo small shifts with temperature. We can then obtain the shift in energy of each point on the phonon DOS curve with temperature through $\partial g/\partial T$ and $\partial g/\partial \epsilon$:

$$\frac{\partial E_{\text{ph}}}{\partial T} = C_V(T) + 3 \int_0^\infty g_T(\epsilon)\frac{-\partial g/\partial T}{\partial g/\partial \epsilon} \left(\frac{1}{2} e^{\epsilon/kT} + 1\right) d\epsilon. \hspace{1cm} (5)$$

[When $\partial g/\partial \epsilon$ is small, it may be important to scale $g(\epsilon)$ by its breadth.] With increasing temperature there are more phonons in the crystal, increasing the total phonon energy. The phonon energies decrease with the volume of the crystal, however, so with increasing temperature it is advantageous to increase slightly the volume of the crystal, even though this creates an elastic energy, $E_{\text{el}}$:

$$E_{\text{el}} = \frac{1}{2} B \alpha (3\alpha T)^2. \hspace{1cm} (6)$$

where $\alpha$ is the linear coefficient of thermal expansion, $B$ is the bulk modulus, and $\nu$ is the specific volume. This decrease in phonon energy is converted into elastic energy so that

$$3 \int_0^\infty g_T(\epsilon)\frac{-\partial g/\partial T}{\partial g/\partial \epsilon} \left(\frac{1}{2} e^{\epsilon/kT} + 1\right) d\epsilon + B\alpha (3\alpha T)^2 T=0. \hspace{1cm} (7)$$

The thermal expansion can be related to the temperature dependence of the phonon DOS through Eq. (7). With the Grüneisen approximation of $\partial \epsilon/\partial \nu = -\gamma \epsilon/\nu$, where $\gamma$ is a constant:

$$\frac{\partial g}{\partial T} = -\frac{\partial g}{\partial \nu} \cdot \frac{\partial \nu}{\partial T} \cdot \frac{\partial T}{\partial \nu}, \hspace{1cm} (8)$$

$$\frac{\partial g}{\partial \nu} = -\frac{\partial g}{\partial \epsilon} \left(-\gamma \frac{\epsilon}{\nu}\right) \cdot (3\alpha). \hspace{1cm} (9)$$

It is easy to substitute Eq. (9) into Eq. (7) and obtain for the Grüneisen approximation at high temperatures

$$\alpha = \gamma \frac{C_V}{3B}. \hspace{1cm} (10)$$

Unfortunately, the Grüneisen approximation is not accurate for the temperature dependence of our experimental $g(\epsilon)$. Our approach to calculating $C_V(T)$ is instead to linearly interpolate the phonon DOS curves of 11 and 300 K, including the zero-point contribution:

$$C_V(T) = \frac{3T}{T_2-T_1} \int_0^\infty \left[g_{T_2}(\epsilon)-g_{T_1}(\epsilon)\right] \frac{\epsilon^2 e^{\epsilon/kT}}{kT^2 (e^{\epsilon/kT}-1)^2} d\epsilon + \frac{3T}{T_2-T_1} \int_0^\infty \left[g_{T_0}(\epsilon)-g_{T_1}(\epsilon)\right] \frac{\epsilon}{2} d\epsilon, \hspace{1cm} (11)$$

where the temperatures are $T_2=300 \text{ K}$ and $T_1=11 \text{ K}$. The phonon DOS at 11 K is assumed to be the same as that of zero temperature.

To obtain $C_p(T)$, we used the result from classical thermodynamics:

$$C_p(T) = C_V(T) + 9B \gamma \alpha^2 T, \hspace{1cm} (12)$$

where the first term is provided by Eq. (11). To obtain $C_p(T)$ from the phonon DOS alone, we obtained the second term from Eq. (7):

$$C_p(T) = \frac{3T}{T_2-T_1} \int_0^\infty \left[g_{T_2}(\epsilon)-g_{T_1}(\epsilon)\right] \frac{\epsilon^2 e^{\epsilon/kT}}{kT^2 (e^{\epsilon/kT}-1)^2} d\epsilon + \frac{3T}{T_2-T_1} \int_0^\infty \left[g_{T_2}(\epsilon)-g_{T_1}(\epsilon)\right] \frac{\epsilon}{2} d\epsilon + \frac{3T}{T_2-T_1} \int_0^\infty \left[g_{T_0}(\epsilon)-g_{T_1}(\epsilon)\right] \frac{\epsilon}{2} d\epsilon. \hspace{1cm} (13)$$

### III. EXPERIMENTAL

Ingots of Ni$_3$V were prepared by the induction melting of pieces of elemental Ni (99.99+%) and V (99.9%) in an argon atmosphere. The ingots were sealed in evacuated quartz ampoules and homogenized at 1150 °C for 2 h and cooled in the furnace. The brittle homogenized ingots were cold-rolled to break them into pieces of about 1 g mass. These small pieces were annealed in evacuated quartz ampoules at 1150 °C, and quenched by breaking the hot ampoule in iced brine. In what follows, we refer to these materials as "partially disordered." To form the equilibrium $D_{022}$ structure, some of these partially disordered pieces were annealed at 850 °C for 2 h and cooled in the furnace; we refer to these materials as "ordered." Samples of both materials were heated to 400 °C and analyzed for evolved hydrogen, oxygen, and nitrogen with a Hewlett-Packard 5890 gas chro-
matograph equipped with a thermal conductivity detector. None of these gases were detected, and detectability limits were 0.0032 wt% for hydrogen, 0.078 wt% for oxygen, and 0.22 wt% for nitrogen. Chemical compositions and chemical homogeneities were measured with a JEOL Superprobe 733 electron microprobe. Averages of the composition measurements gave 25.44 ± 5% for the partially disordered alloy, and 25.39 ± 5% for the ordered alloy. Composition variations within each sample were no more than about 0.1 at%. X-ray diffractometry was performed with an Inel CPS-120 diffractometer using Cu Kα radiation, and an Al filter was used to suppress V Kα fluorescence.

Low-temperature heat-capacity measurements employed a Perkin-Elmer DSC-4 differential scanning calorimeter (DSC) that had been modified by installing its sample head in a liquid-helium dewar. Masses (about 300 mg) of the partially disordered and ordered alloys were matched to 0.1 mg accuracy and placed in the two sample pans of the DSC. Heat-capacity measurements comprised pairs of runs, with the two samples interchanged in their sample pans between runs. The difference in heat capacities of the two samples was obtained from the difference of these two sets of runs. To test reproducibility, we obtained nine matched pairs of runs with liquid nitrogen, and two matched pairs with liquid helium as the cryogen. To counteract instrumental drift, runs comprised typically overlapped by 10 K. Scans were performed at 10 and 20 K min⁻¹. A measurement was also performed with the ordered sample alone to determine approximately its Debye temperature. Thermal-expansion measurements were performed over a temperature range from 50 to 275 °C using a Perkin-Elmer TMA7.

Efforts were made to measure ultrasonically the longitudinal and shear wave velocities in the partially disordered and ordered states of Ni₃V. We used a Panametrics 10 MHz ultrasonic longitudinal wave transducer and a Panametrics 5 MHz ultrasonic shear wave transducer, whose outputs were passed through a Panametrics Model 5052UA ultrasonic analyzer to a Hewlett Packard 54510A oscilloscope sampling at 1 GHz. Two sets of matched cylindrical samples were used. The top and bottom faces of the cylinders were accurately cut parallel and then polished. Successful measurements of the longitudinal and shear wave speeds in Cu₃Au were made using similar samples from previous calorimetry measurements. We deduced bulk moduli at room temperature of 18.88 × 10¹⁰ Pa for L1₂-ordered Cu₃Au, and 18.70 × 10¹⁰ Pa for chemically disordered fcc Cu₃Au, in good agreement with previous results. However, none of the Ni₃V samples showed a pulse-echo pattern, so measurements were impossible. The samples of Ni₃V evidently showed a strong ultrasonic attenuation, perhaps because inhomogeneous internal stresses caused scattering of the ultrasonic waves.

To measure Young’s moduli, compression tests were performed using an Instron Model 4204 load frame. A cylindrical sample of 0.55 cm diameter and 1.9 cm height was machined from an induction-melted ingot of Ni₃V, and was heat treated to produce the partially disordered state. After compression testing, the same sample was annealed for 2 h at 850 °C and cooled in the furnace to obtain the ordered state, and the compression tests were repeated. The crosshead speed was 0.05 cm/min, and the extension of the sample was measured using a strain-gauge extensometer. We attempted to perform the compression tests in the elastic regime of the material. The yield stress at room temperature for ordered Ni₃V has been reported to be 900 MPa. Our samples were loaded to only 270 MPa, and we ensured that there was no reduction in slope of the stress-strain curves at the highest loads. Several load-unload cycles were performed on each sample. We also performed compression tests on a similar sample of mild steel to confirm that we obtained a reasonable Young’s modulus and no hysteresis in our stress-strain measurements.

Samples of the partially disordered and ordered alloys, each about 50 g, were placed in thin-walled aluminum cans and mounted in a closed-cycle helium refrigerator on the goniometer of the HB2 triple-axis spectrometer at the High Flux Isotope Reactor at the Oak Ridge National Laboratory. Measurements on our two materials were performed at both 11 and 300 K. The spectrometer was operated in constant-Q mode with the fixed final energy E_f of 14.8 meV. The energy-loss spectra were made by scanning the incident energy from 14.8 to 74.8 meV. The neutron flux from the monochromator was monitored with a fission detector, which was used to control the counting time for each data point. The incident beam on the pyrolytic graphite monochromator crystal had a collimation of 71°, and 5° Soller slits were used between the monochromator and the sample. Pyrolytic graphite filters placed after the sample were used to attenuate the λ/2 and λ/3 contamination. The filtered beam passed through 3° slits before the pyrolytic graphite analyzer crystal. Following the analyzer, 7° Soller slits were used before the 4He detector. With this arrangement, the energy resolution varied between 0.9 and 2 meV, depending on the energy transfer and the slope of the phonon dispersion surface. Spectra from each specimen were obtained at four values of Q: 3.48, 3.73, 3.98, and 4.23 Å⁻¹.

IV. RESULTS

A. Structure

Very weak, if any, superlattice diffraction peaks were observed in the Co Kα x-ray-diffraction patterns from any samples, but the x-ray form factors are not strongly different for Ni and V atoms. On the other hand, neutron diffraction showed strong superlattice diffraction peaks from both the quenched sample and the annealed sample [e.g., the (002), (101), (110) peaks at q = 1.74, 1.98, 2.51 Å⁻¹]. From calculated peak intensities, we found the ordered alloy to have a long-range order (LRO) parameter close to one. The superlattice peaks from the quenched samples were broadened, but had 85 to 90% of the areas of the superlattice peaks from the annealed sample. The Bragg-Williams LRO parameter of the quenched alloy was therefore between 0.90 and 0.95. X-ray and neutron powder diffraction profiles showed tetragonality in the annealed specimen that was characteristic of the D0₂₂ structure. Figure 1 shows that the ratio of the intensities of the (200) and (020) diffractions (at q = 3.48 and 3.55 Å⁻¹) are 1:2, as expected for the powder-averaged intensities of these diffractions. The as-quenched specimens showed no tetragonality, and their sharp diffraction peaks were characteristic of an fcc structure. This is consistent with previous
results of transmission electron microscopy studies that showed a "tweed" microstructure of quenched Ni$_3$V. The tweed microstructure has a fine-scale distribution of internal strains, but no regions that are distinctly tetragonal.\textsuperscript{17,21,22} Since the quenched sample had a high degree of the chemical order of the $D_{022}$ structure, but none of the long-range tetragonality, we call it partially disordered.

### B. Calorimetry

Averaged results from the differential calorimetry measurements are presented in Fig. 2. The sign of the data is positive, showing that Ni$_3$V has a larger heat capacity in the partially disordered state than in the ordered state. The heat capacity was also measured with an ordered sample alone. From this experiment the Debye temperature was determined to be approximately 365 K. [This could be inaccurate, since data were not obtained much below 100 K, but it showed reasonable agreement with the heat capacity calculated with the phonon DOS curves as described below, and should be adequate for our need to account for the low-temperature part of $\Delta C_p(T)$ for use in Eq. (1).] Using this Debye temperature of 365 K for the ordered sample, the data of Fig. 2 could be best fit at temperatures below 160 K with a Debye temperature of 360 K for the partially disordered sample. At high temperatures, these Debye temperatures provide a larger vibrational entropy for the partially disordered than the ordered alloy, and $\Delta S_{\text{vib}}$ is

$$\Delta S_{\text{vib}} = 3k_B \ln \left( \frac{365}{360} \right) = 0.041 \ k_B / \text{atom.} \quad (14)$$

### C. Elastic moduli, thermal-expansion coefficients, Grüneisen constants

The stress-strain curves of Fig. 3 show considerable hysteresis. For determining the Young’s modulus we used the unloading curve at stresses slightly below the peak stress of the test. We expect this slope to be least affected by internal processes contributing to hysteresis, and more representative of the elastic response. In support of this expectation, we found that the unloading curve was more reproducible than the loading curve, and we found that the Young’s modulus of the ordered material was in good agreement with that ofFrançois, Hug, and Veyssière.\textsuperscript{18} Young’s moduli are presented in Table I, together with linear coefficients of thermal expansion.

Grüneisen constants were obtained from the temperature dependence of the phonon DOS. For the ordered alloy, for example, we rescaled in energy the 300 K phonon DOS curves by 0.95% to achieve a best match with the 11 K curve. The 300 K curve for the partially disordered alloy matched best with the 11 K curve for a rescaling by 1.5%. Using the linear coefficients of thermal expansion in Table I with the 289 K difference between 11 and 300 K, we obtain the Grüneisen constants $\gamma$ of 4.9 for the partially disordered alloy and 3.2 for the ordered alloy. These values seem large, perhaps because the measured thermal contraction is an average of anisotropic constants involving different crystallographic directions. On the other hand, using Eq. (10) we obtain Grüneisen constants of 1.15 for the partially disordered material and 1.53 for the ordered material. Not only are these Grüneisen constants smaller that those obtained from the phonon DOS, but their relative sizes are reversed for the two mate-

### Table I. Measured physical properties of partially disordered and ordered Ni$_3$V.

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<thead>
<tr>
<th>State of Ni$_3$V</th>
<th>Young’s modulus ($\times 10^{10}$ Pa)</th>
<th>$\alpha$ (350 K)</th>
<th>$\gamma$ [from Eq. (10)]</th>
<th>$\gamma$ (from DOS)</th>
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<tbody>
<tr>
<td>Partially disordered</td>
<td>12.4</td>
<td>10.6 $\times 10^{-6}$ K$^{-1}$</td>
<td>1.15</td>
<td>4.9</td>
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<tr>
<td>$D_{022}$ ordered</td>
<td>17.2</td>
<td>10.2 $\times 10^{-6}$ K$^{-1}$</td>
<td>1.53</td>
<td>3.2</td>
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rials. We believe that the inconsistency in these Grüneisen constants is caused by the crystallographic anisotropy of Ni$_3$V.

D. Inelastic neutron scattering

The 16 inelastic-scattering spectra from the two samples (partially disordered and ordered), at two temperatures (11 and 300 K), and four values of $Q$ (3.48, 3.73, 3.98, 4.23 Å$^{-1}$), are presented in Fig. 4. The strong elastic peak is seen at energies below 2 meV. At higher energy losses, the inelastic scattering shows features of the phonon DOS of the material, such as the peak from the longitudinal branch at 33 meV. In each of these spectra, the phonon DOS is significantly modified by a thermal factor and the $Q$ dependence of the coherent inelastic scattering. Since all spectra were obtained with the same total incident beam flux, the thermal factor is evident from the stronger scattering at 300 than at 11 K. The $Q$ dependence of the coherent inelastic scattering is seen as differences in the shapes of the four spectra in each of the four graphs of Fig. 4. Overlays of these raw data show that the inelastic loss spectra of the ordered alloy are at slightly higher energies than are spectra of the disordered alloy, and the inelastic loss spectra of both materials show some thermal softening.

We proceeded to analyze these data to extract four phonon DOS curves for the two samples, partially disordered and ordered, at two temperatures, 11 and 300 K. Our method has similarities to approaches used previously.$^{10,23-25}$ To understand the effect of temperature, we calculated the incoherent inelastic scattering using the conventional multiphonon expansion.$^{26-28}$ The calculation was performed for 300 K with the phonon DOS curve of fcc Ni.$^{10,29,30}$ The results showed that at the relatively low values of $Q$ and temperature of the present experiments, the inelastic scattering is strongly dominated by one-phonon processes, but the small background enhancement of the 300 K data with respect to the 11 K data was approximately consistent with the calculated two phonon scattering. First, a background was stripped from each spectrum. Second, each spectrum was corrected by the one-phonon thermal factor, $f(T)$, of the form:

$$f(T) = 1 - \exp(-e/kT).$$

All spectra were then normalized to unit area. Finally, for each specimen at each temperature, we summed all four spectra for the different values of $Q$. For the incoherent inelastic part of the scattering, this data processing procedure should provide the total phonon DOS, since the incoherent scattering from both Ni and V atoms is the same. The coherent inelastic scattering from Ni atoms contributes significantly to the spectra, however.

It is usually not possible to obtain an accurate phonon DOS from coherent inelastic scattering spectra of polycrystals without prior knowledge of the lattice dynamics of the material,$^{31}$ and there is little such knowledge for Ni$_3$V. One problem occurs because Ni and V atoms have different coherent scattering cross sections. In particular, we were concerned initially that the negligible coherent scattering from V atoms will deemphasize vibrational modes having polarization eigenvectors with large components for V atoms. High-frequency optical modes should be particularly susceptible to this problem. However, if there were significant differences between samples in vibrational modes emphasizing V atoms, we should be able to detect the differences through changes in the incoherent inelastic scattering. Furthermore, most optical modes involve some motion of Ni atoms that are neighbors of the V atoms, so these modes should also contribute to the coherent inelastic scattering. We examined carefully the spectra in Fig. 4 and the final DOS curves of Fig. 5 over the energy range of 25–50 meV. We found no distinct differences in the features of curves for the four sets of data.

The processed phonon DOS curves are very similar to each other, and to the phonon DOS curve for fcc Ni.$^{10}$ In our previous work,$^{10}$ a Born–von Kármán model was used with interatomic force constants of fcc Ni to calculate the eigenfrequencies and eigenvectors of the dynamical matrix. With this information for each phonon in the first Brillouin zone, the coherent inelastic scattering was calculated by performing a crystallographic average of the dynamical structure fac-
tor intensity at explicit values of \( Q \) with respect to the crystallographic axes. It was shown that for fcc Ni, summing the dynamical structure factors for the four values of \( Q \) (3.48, 3.73, 3.98, 4.23 Å\(^{-1}\)) provides a good approximation to the phonon DOS.\(^{10}\) More significantly, systematic errors in the analysis are not too important for our purposes, since our need is to identify differences in the phonon DOS curves for the different states of the material.

Owing to the excellent 0.01 meV energy accuracy and stability of the HB2 spectrometer, small energy shifts in the phonon DOS curves can be measured reliably. It is seen in Fig. 5 that the curve for the ordered alloy at 11 K is shifted to the highest energy, and the lowest curve is for the disordered alloy at 300 K. Differences in the partially disordered and ordered DOS curves at the same temperature are indicative of the harmonic contribution to the difference in vibrational entropy between the two materials, and the changes of these differences with temperature are indicative of anharmonic effects on the difference in vibrational entropy.

\[ \Delta C_v(T) = C_{v,PD}(T) - C_{v,0}(T) \]

\[ \Delta C_p(T) = C_{p,PD}(T) - C_{p,0}(T) \]

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considering that there are no adjustable parameters in correlating the results from two very different sets of measurements—inelastic neutron scattering and differential calorimetry.

Thermal expansion was calculated from the phonon DOS curves by arranging Eq. (7) to solve for $a$. At 300 K, we obtained linear coefficients of thermal expansion of $15.5 \times 10^{-6}/K$ for the partially disordered alloy, and $13.7 \times 10^{-6}/K$ for the ordered alloy. These results seem reasonable, but we note that they would be more accurate if we used the larger bulk modulus obtained by electronic structure calculations$^{32,33}$ rather than the data of Table I.

**B. Microstructure and elastic energy**

Although the $\Delta C_p(T)$ calculated by our second attempt in Sec. VA with Eq. (13) was successful, the $\Delta C_p(T)$ calculated by our first attempt with Eq. (12) was qualitatively unsuccessful. We believe the problem in using Eq. (12) originates with our measured bulk moduli. We propose a microstructural mechanism for elastic energy storage in polycrystalline Ni$_3$V with the DO$_{22}$ structure which allows for macroscopic differences in the bulk moduli of the two samples, even though they have nearly the same local chemical order. The mechanism is based on the tetragonal anisotropy of the thermal expansion of the ordered alloy. For Ni$_3$V with DO$_{22}$ order, it is known that the microstructure within each prior fcc crystallite consists of lenticular packets comprising lamellas of ordered domains. The domains are mutually arranged in a microtwin-type microstructure to minimize the elastic energy.$^{17,18,21,22}$ Such a microstructure can be optimized to minimize elastic energy at only one temperature, however. With changes in temperature, the ordered domains expand or contract anisotropically, generating internal elastic energy owing to geometrical mismatch between the lenticular packets. The ordered domains were originally formed during the annealing and cooling from 850 °C, so we expect the microstructure was optimized for minimizing elastic energy at high temperatures. Anisotropic thermal contraction upon cooling will generate internal stresses at room temperature. Tanner showed that the tetragonality of ordered Ni$_3$V can vary from about 1 to 2 %, depending on the thermal processing.$^{17}$ (Our ordered alloy had a tetragonality of 1.7%). Nonequilibrium tetragonality requires the presence of internal stresses. In Tanner’s work, significant strain contrast was found in transmission electron micrographs of ordered Ni$_3$V at room temperature, and others have reported large strain effects around Ni$_3$V precipitates in Ni-V alloys.$^{21,22}$ In comparison, crystals of the disordered alloy have little or no tetragonality. Since the partially disordered alloys have a high degree of chemical order, however, they must have significant stored elastic energy at all temperatures. These local elastic distortions cause “tweed” diffraction contrast in TEM. We do not know the temperature dependence of these elastic distortions in the partially disordered alloy, although it is likely that they change with temperature.

We expect this microstructural mechanism for elastic energy storage in the polycrystalline ordered alloy to affect the elastic moduli measured in tests on macroscopic specimens. We expect the measured bulk modulus, $B = V \frac{\partial^2 E}{\partial V^2}$, to depend in the usual way on the energy of the crystal origi-
reasonable to calculate the temperature dependence of the difference in microstructural heat capacities: 

\[ \Delta C_{p\text{stat}}(T) = C_{p\text{stat}}^\text{PD}(T) - C_{p\text{stat}}(T) \].

This temperature dependence is presented (probably with its opposite sign) in Fig. 6. It is perhaps not surprising that adding an appropriately scaled \( \Delta C_{p\text{stat}}(T) \) to the \( \Delta C_p(T) \) calculated from the phonon DOS curves in Sec. V A can improve the quality of fit to the experimental data. The improvement in the fit was not large enough to make a convincing case for the size of \( \Delta C_{p\text{stat}}(T) \), however. By assuming the difference in \( B' \) is the measured difference in Young’s moduli (Table I), from Eq. (19) we obtain a difference in elastic energy of about 100 J/mol at low temperatures, with the ordered alloy having the larger elastic energy. This estimate shows that \( \Delta C_{p\text{stat}}(T) \) could be comparable to the other contributions presented in Fig. 6. Unfortunately, although we expect that \( \Delta C_{p\text{stat}}(T) \) is a real phenomenon, its quantitative evaluation is not justified given the accuracy of our calorimetry data and the uncertainty in the calculated anharmonic part of \( \Delta C_{p\text{stat}}(T) \). Furthermore, the thermal contraction of the ordered material upon cooling from 1123 to 160 K is large, being about 1%. With anisotropic contractions, it is likely that the elastic contractions may give way to some local internal plastic deformation at the lowest temperatures. Plastic deformation in the ordered alloy could alter \( \Delta C_{p\text{stat}}(T) \) at the low temperatures.

**C. Microstructure and plastic deformation**

The ordered Ni$_3$V does not exhibit ideally elastic behavior, as shown by the mechanical hysteresis of Fig. 3. The area of the loop is largest for the first few cycles, but the loop remains relatively constant after the first cycle shown in Fig. 3. The area of the loop increases strongly with the maximum strain. We are confident that the data of Fig. 3 show the hysteretic loss of mechanical energy in the ordered alloy is greater than in the partially disordered alloy (for which the maximum strain was larger, but the area of the loop is smaller). In a cyclic process, the mechanical deformation of the ordered alloy should be more strongly converted into heat. The area of the particular hysteresis loop shown for the ordered alloy in Fig. 3 corresponds to 0.6 J/mole, which seems too small to account for the large anharmonic effects in Fig. 2.

We are still investigating the origin of the large mechanical hysteresis in the ordered Ni$_3$V. The hysteretic behavior of the ordered alloy could be promoted by the internal stresses from thermal contraction, which may be nearly large enough to drive plastic deformation at some locations in the microstructure. It is also possible that hysteretic effects may arise if the axes of tetragonality of the D0$_{22}$ structure change to accommodate the applied stress. We have performed preliminary measurements of x-ray diffraction patterns when the sample was under a compressive strain of about 0.2%. We found no evidence of transformations between variants of the D0$_{22}$ structure at this strain, however.

**D. Entropy**

Using the curve labeled DOS \( C_V(T) \) in Fig. 6, we used Eq. (1) to calculate the difference in vibrational entropy of the partially disordered and ordered Ni$_3$V to be 0.025 k$_B$/atom at 300 K, with the partially disordered material having the higher entropy. This calculated heat-capacity curve does lie below the experimental data at low temperatures, and above at higher temperatures. To make the estimate of the difference in vibrational entropy more consistent with the calorimetry data, we increased the curve DOS \( \Delta C_V(T) \), and decreased the curve DOS Anharmonic, and with the sum of these new curves in Eq. (1) we obtained the same value of \( \Delta S_{\text{vib}}(T) = (0.038 \pm 0.015)k_B/\text{atom} \) at 300 K. The anharmonic contribution to the heat capacity provides a thermal increase of the difference in vibrational entropy of 5.84 x 10$^{-5}$ k$_B$/atom K$^{-1}$. This difference in vibrational entropy between the partially disordered and ordered states of Ni$_3$V is smaller than results reported for other alloys.$^5$ We believe the reason is that our partially disordered Ni$_3$V had nearly the same chemical long-range order as did our ordered Ni$_3$V.

**VI. CONCLUSIONS**

We performed a comparative study of two states of Ni$_3$V, a state of partial disorder obtained by rapid quenching, and the state of equilibrium D0$_{22}$ order obtained by annealing. The heat capacity of the partially disordered alloy was consistently larger than that of the ordered alloy in the temperature range of our calorimetry measurements, 60–325 K. Inelastic neutron scattering was used to obtain approximate phonon density of states curves for the two alloys at 11 and 300 K. The phonon energies were larger for the ordered alloy than the disordered alloy, as expected from their difference in heat capacities. The \( C_V(T) \) calculated from the phonon DOS curves measured at 11 K could account for most of the difference in heat capacities of the two materials at temperatures below 160 K.

The phonon DOS curves showed thermal softening between 11 and 300 K. The phonon DOS of the partially disordered alloy showed more thermal softening than the ordered alloy, and this softening could account for much of the differential anharmonic heat capacity of the two states of Ni$_3$V at the higher temperatures.

We performed ancillary measurements of the linear coefficients of thermal expansion and the Young’s moduli of the two alloys. The thermal expansion coefficients could be calculated from the temperature dependencies of the phonon DOS curves. There was a significant difference in the Young’s moduli of the two alloys, however. With these moduli the classical anharmonic contribution, \( C_p(T) - C_V(T) = 9B'\alpha^2T \), predicted the wrong sign of the measured anharmonic contribution. This suggests that some of the anharmonic heat capacity could arise from a microstructural contribution. When the alloy is cooled from the high temperature where the ordered domains are formed, anisotropic thermal contractions cause the buildup of elastic energy in the ordered alloy. With increasing temperature, this elastic energy is relieved and converted into heat, suppressing the measured heat capacity. Our present data are unfortunately insufficient to isolate rigorously this microstructural contribution to the heat capacity. There may be another small microstructural contribution to the anharmonic heat capacity originating with the hysteretic mechanical behavior of ordered Ni$_3$V.

For the partially disordered and ordered alloys, we estimate the difference in vibrational entropy to be \( \Delta S_{\text{vib}}(T) = (0.038 \pm 0.015)k_B/\text{atom} \) at 300 K. The anharmonic contribution to the heat capacity provides a thermal increase of the difference in vibrational entropy with temperature of
the amount \(5.84 \times 10^{-3} k_B \) atom\(^{-1} \) K\(^{-1}\). The difference in the elastic energy in the microstructure is about 100 J/mol at low temperatures, and may make a significant contribution to the difference in heat capacity of the partially disordered and ordered alloys.

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