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Phonon contributions to the entropies of $hP24$ and fcc Co$_3$V

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Inelastic neutron-scattering spectra and neutron-diffraction patterns were measured on the alloy Co$_3$V at temperatures from 1073–1513 K, where the $hP24$ (ordered hexagonal) and fcc structures are the equilibrium states of the alloy. Phonon density of states (DOS) curves were calculated from the inelastic-scattering spectra, allowing estimates of the vibrational entropy in the harmonic and quasiharmonic approximations. The vibrational entropy of the $hP24$–fcc phase transition at 1323 K was found to be $0.07k_B$/atom. The anharmonic contributions to the entropy over a temperature range of 100 K were comparable to the vibrational entropy of this phase transition. The anharmonic softening of the phonon DOS was only slightly larger for the $hP24$ than the fcc phase, however, so the anharmonic effects contribute only slightly to the difference in entropy of the two phases. The simple Grüneisen approximation was inadequate for predicting the thermal softening of the phonon DOS. [S0163-1829(99)07637-7]

I. INTRODUCTION

Experimental measurements of the vibrational entropy differences of alloy phases[1-3] have motivated a number of theoretical studies in the last year or so.[4-10] One of the important results from these recent calculations is that the phonon density of states (DOS) is quite sensitive to the lattice parameter. Recent experiments have also shown how temperature, presumably through thermal expansion, alters significantly the phonon DOS of solid phases.[11,12] These changes will have thermodynamic importance if they differ for two phases of an alloy. Differences in lattice parameter have been argued to affect differences in vibrational entropies of ordered and disordered Cu$_3$Au (Refs. 9 and 13) and Ni$_3$Al (Refs. 6–8). These results indicate that for determining the vibrational entropy of phase transitions, the phonon DOS should be obtained at temperatures near the phase transition itself.

The alloy Co$_3$V is advantageous for neutron inelastic-scattering measurements of phonon DOS, in part because Co and V atoms have ratios of σ/m that differ by only 5%, where σ is the total scattering cross section and m is the atomic mass. The Co and V nuclei therefore have similar cross sections for the scattering of neutrons by phonons. Furthermore, the scattering from Co and V is largely incoherent. This facilitates the conversion of the inelastic-scattering spectra into phonon DOS curves, since features of the incoherent inelastic scattering spectra do not depend on the experimental momentum transfer Q. This independence of the spectral shape on Q was confirmed experimentally in our recent measurements on Co$_3$V.[11]

Our previous measurements of the phonon DOS of Co$_3$V (Ref. 11) showed a significant thermal softening of the phonons in the low-temperature $hP24$ phase (a hexagonal ordered intermetallic compound of space group $P\bar{6}m2$). The change in DOS over a temperature range of 200 K was comparable to the change across the $hP24$–fcc phase transition at 1320 K. The thermal softening of the phonon DOS was not measured for the high-temperature fcc phase, however, so the anharmonic contribution to the difference in entropy of the $hP24$ and fcc phases was not determined. (It is this difference that affects the thermodynamics the $hP24$–fcc phase transition.) Unfortunately, the temperatures at which the measurements were made in the previous work were based on erroneous information about the Co-V phase diagram, which included an $L1_2$ phase (Cu$_3$Au structure) from 1298–1343 K. This phase was shown to be a transient state in the quenched fcc structure,[14] and the $hP24$ phase undergoes a phase transition directly to the fcc phase at 1320 K. With this more recent information on the Co-V phase diagram, we repeated some of the previous measurements so the phonon DOS could be measured closer to the temperature of the $hP24$–fcc phase transition. In the present work we also measured the temperature dependence of the inelastic scattering from the high-temperature fcc phase. Finally, we performed a series of neutron-diffraction measurements to measure lattice parameters and to determine if there was any chemical disordering of the $hP24$ phase at temperatures below the transition to the fcc solid solution.

The present neutron-diffraction measurements showed that the phase transition between the low-temperature $hP24$ phase and the fcc phase occurs abruptly at about 1323 K, with no significant change in the long-range chemical order of the $hP24$ phase below this temperature. The significant phonon softening reported for the $hP24$ phase[11] was confirmed, and a similar softening was found for the fcc phase.

There is an approximate, but incomplete, cancellation of anharmonic effects on the vibrational entropy of the $hP24$–fcc phase transition. Most of the difference in vibrational entropy of the $hP24$ and fcc phases can be understood with a harmonic interpretation using the phonon DOS curves at temperatures just across the phase-transition temperature. This difference in vibrational entropy is $0.07k_B$/atom, which is almost certainly smaller than the difference in configurational entropy between the chemically ordered $hP24$ phase and the disordered fcc solid solution. Finally, the temperature dependence of the phonon DOS was shown to be in poor agreement with predictions of a simple Grüneisen model of phonon softening.

II. EXPERIMENTAL

Pellets of Co_3V for inelastic neutron-scattering studies were prepared at the Materials Preparation Center, Ames Laboratory, Ames, Iowa. The preparation and chemical purity of this alloy were described previously.[11] The pellets were placed in vanadium cans of 9 mm inner diameter and 6 cm in length. No Gd spacer disks were used for this set of measurements. The sample cans were mounted in a high-temperature furnace, which was kept under high vacuum throughout the experiment. Neutron-diffraction data were measured with the HB4 high-resolution powder diffractometer at the High-Flux Isotope Reactor at ORNL, using an incident neutron wavelength of 0.150 nm. Eleven diffraction patterns were acquired at temperatures from 1073–1503 K. A Rietveld refinement analysis using the GSAS package[15] was used to obtain lattice parameters, but the Debye-Waller factors could not be determined reliably owing to changes in crystallographic texture in the samples during heating in the furnace.

For the inelastic-scattering measurements, the furnace was transferred to the goniometer of the HB3 triple axis spectrometer. The spectrometer was operated in constant-Q mode with a fixed final energy of 14.8 meV. The configuration was as described previously,[11] and it was confirmed that the instrument intensity and resolution were nearly identical to those of the previous runs. Runs were performed at only one value of Q, 46.0 nm^{-1}, which was nearly the highest value of Q accessible with our configuration of the HB3 spectrometer.

III. RESULTS

Three neutron-diffraction patterns are presented in Fig. 1. The measurements were first performed at lower temperatures where the sample had the $hP24$ structure. From previous work we found that the initial $L1_2$ (metastable) structure of the quenched pellets had transformed to the $hP24$ structure around 1000 K. The diffraction pattern at the bottom of Fig. 1 shows that the sample had the $hP24$ structure at 1073 K. This diffraction pattern includes some peaks corresponding to interplanary spacings of the twinned fcc structure that provides the underlying atom positions of the $hP24$ structure,[14] plus smaller peaks characteristic of long-range chemical order on this underlying structure. The intensities of these smaller peaks did not change significantly when the sample temperature was increased from 1073–1318 K, just
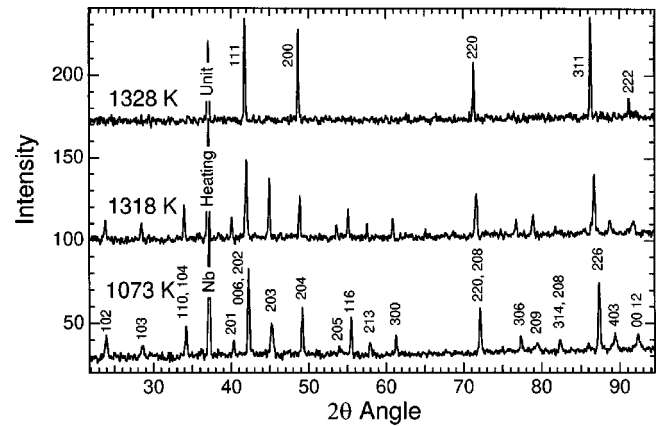

FIG. 1. Neutron-diffraction patterns from Co_3V measured at the temperatures indicated, showing an fcc pattern (cubic indexing) at 1328 K and $hp24$ patterns (hexagonal indexing) at 1318 and 1373 K.

below the temperature of the $hP24$–fcc phase transition. This indicates that at 1318 K the sample was single-phase $hP24$, but confirmation with the GSAS package was not practical owing to the crystallographic texture of the sample, and the evolution of this texture during the measurements. At least some of these smaller peaks became sharper when the sample temperature was heated from 1073–1318 K, however, suggesting that the $hP24$ phase formed initially as small domains within the $L1_2$ structure. (See the peak indexed as 203 at $2\theta=45°$, for example. The quality of our diffraction line shapes is, unfortunately, inadequate to identify the morphology or orientation of the $hP24$ domains.) Figure 1 shows that between 1318 and 1328 K the sample has transformed fully to a single-phase fcc structure with no observable chemical long-range order. Our previous estimate of this phase-transition temperature was 1318 K,[14] but the present data suggest it is 5 K higher.

The Rietveld refinement analyses of the diffraction patterns were used to obtain the temperature dependences of the lattice parameters. The c-axis parameter for the $hP24$ phase was anomalously large at 1073 K, and at this temperature the diffraction peaks were broad. We believe these features are associated with the nucleation of small domains of $hP24$ phase within the initial $L1_2$ phase of the as-received material, and this is the subject of ongoing investigation. Neglecting this one datum at 1073 K, and using c-axis parameters from five diffraction patterns from 1223 to 1318 K, we found that the linear coefficient of thermal expansion for the c axis was indistinguishable from that of the a axis of the $hP24$ phase. The linear coefficients of thermal expansion were determined to be $(24.9\pm1.0)\times10^{-6}$ K^{-1} for the $hP24$ phase at an average temperature of 1270 K, and $(24.1\pm0.5)\times10^{-6}$ K^{-1} for the fcc phase at an average temperature of 1425 K. Although these thermal expansion coefficients are the same within experimental error, it was found previously that the thermal expansion had a significant dependence on temperature for the $hP24$ phase. Over a range of 155 K, the thermal expansion of the $hP24$ phase will change by 1.7 $\times10^{-6}$ [Eq. (1) in Ref. 11]. We therefore believe the $hP24$ phase to have a linear coefficient of thermal expansion that is about $11\pm5\%$ larger than that of the fcc phase at 1425 K.
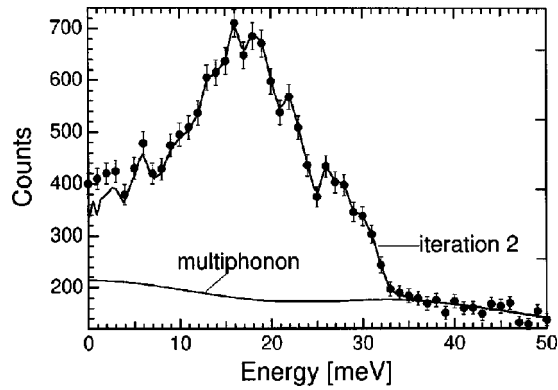
FIG. 2. Points: inelastic neutron-scattering spectrum acquired at 1308 K. Curves: calculated total scattering and multiphonon component, obtained from the phonon DOS from the first full iteration (see text, Sec. III).

A typical inelastic neutron-scattering spectrum in presented in Fig. 2. The data analysis was described in detail previously,[11] but some intermediate steps are shown in Fig. 2. To convert inelastic-scattering measurements at elevated temperatures to a phonon DOS, it is necessary to correct the data for multiphonon scattering. When the multiphonon scattering is known and subtracted from the measured spectrum, the remaining one-phonon contribution can be transformed easily to a phonon DOS by multiplying by a simple function that includes energy and a thermal correction for phonon occupancies. We performed these multiphonon corrections iteratively. The initial ''guess'' at the phonon DOS was obtained from the experimental data by treating the multiphonon contribution as a constant background. It turns out that this initial guess at the phonon DOS was nearly adequate itself, but the data analysis proceeded for two more iterations. The multiphonon contribution shown in Fig. 2 was obtained after the first full iteration of the phonon DOS (using the DOS one step beyond the initial guess). At least as important as the multiphonon correction was the proper handling of the background correction. In matching the experimental and calculated scattering in Fig. 2, the experimental spectrum was shifted vertically down the y axis by a constant. This constant was used as a background that was subtracted from the data. Perhaps the most delicate part of this procedure is the identification of the break between one-phonon and two-phonon scattering at 33 meV. This region of the spectrum is multiplied by a large factor for the phonon occupancy correction, so errors in the background are magnified. For several temperatures we measured the intensity around 33 meV for additional counting time to improve statistics. The error bars from counting statistics will propagate to the final DOS curves. The fractional size of the error bar to a point on a final phonon DOS curve will equal the ratio of the error in a data point in Fig. 2 to the difference between the data point and its multiphonon background as presented in Fig. 2.

IV. DISCUSSION

Figure 3 presents and compares a total of four phonon DOS curves, obtained after two full iterations of multiphonon, background, and thermal corrections to the experi-
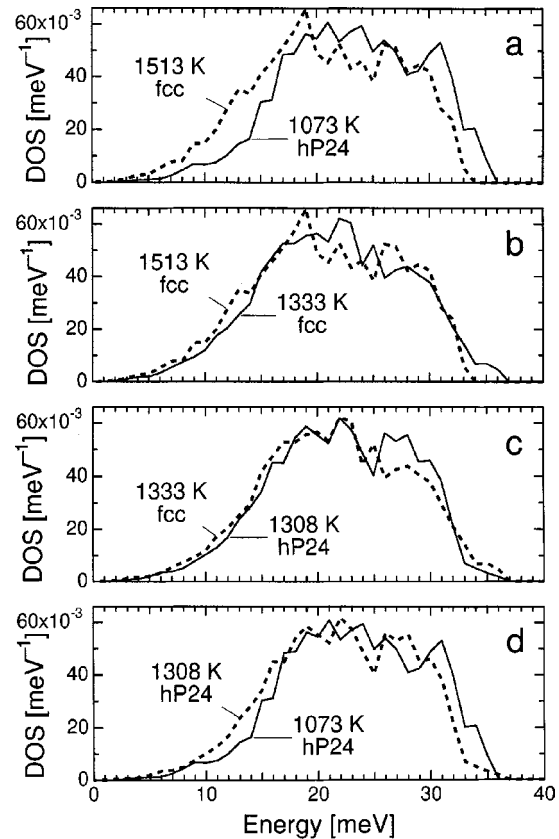

FIG. 3. Phonon DOS curves obtained from Co_3V at the temperatures indicated. These curves, normalized to unity, were obtained after two full iterations of the multiphonon, background, and thermal corrections.

mental spectra. Figure 3(a) compares the phonon DOS curves measured at the lowest and highest temperatures. Figure 3(b) shows the phonon DOS curves of the fcc phase at two temperatures, Fig. 3(c) shows the DOS curves at temperatures just above and below the $hP24$–fcc phase transition, and Fig. 3(d) compares the phonon DOS curves of the $hP24$ phase at two temperatures. The similarity of the comparisons in Figs. 3(b)–3(d) is interesting—the thermal softenings of the phonon DOS curves of the $hP24$ [Fig. 3(d)] and fcc [Fig. 3(b)] phases are at least as large as the change in phonon DOS across the $hP24$–fcc phase boundary [Fig. 3(c)]. All three comparisons show differences in the DOS at low energies from 5–20 meV.

The vibrational entropy of a solid increases with temperature, owing to larger thermal occupancies of phonon states. For a harmonic solid in the high-temperature (classical) limit, an increase in temperature of ΔT causes the entropy of any phase to increase with temperature as $3k_B \Delta T$ per atom. There is no effect of temperature on the difference in the vibrational entropy of different phases. This is not true, however, for anharmonic solids that undergo a thermal softening of their phonon DOS. To calculate this effect, we assume that the phonon frequencies depend on temperature only through thermal expansion. When this is true, it is possible to construct a free energy for the phonons that includes an enthalpy term involving the work done by thermal expansion against the bulk modulus, and a phonon entropy that in-
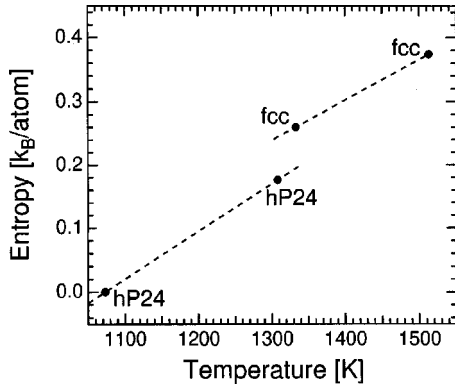
FIG. 4. Differences in vibrational entropy obtained from the measured phonon DOS curves in Fig. 3, using the high-temperature limit of Eq. (3).

creases with softening of the phonon frequencies. Softening of the phonon DOS is unfavorable at low temperatures, since the thermal expansion does work against the bulk modulus. At higher temperatures, however, the increase in vibrational entropy accompanying the softening of the phonon DOS will favor some thermal expansion. In equilibrium this model provides

$$9Bv\alpha^2 = \frac{dS_{\text{vib}}^{\text{anh}}}{dT}, \qquad (1)$$

where $dS_{\text{vib}}^{\text{anh}}/dT$ is the increase with temperature of that part of the vibrational entropy caused by phonon softening. The bulk modulus B, specific volume v, and linear coefficient of thermal expansion α, are all evaluated at temperature T. The softening of the phonon DOS over a range of temperature provides $dS_{\text{vib}}^{\text{anh}}/dT$:

$$\frac{dS_{\text{vib}}^{\text{anh}}}{dT} = \frac{3k_B}{T_2 - T_1} \int_0^\infty (g_1(\varepsilon) - g_2(\varepsilon)) \ln(\varepsilon) d\varepsilon, \qquad (2)$$

where $g_1(\varepsilon)$ is the phonon DOS measured at the temperature T_1. For a small range in temperature, the anharmonic contribution to the vibrational entropy $\Delta S_{\text{vib}}^{\text{anh}}$ is

$$\Delta S_{\text{vib}}^{\text{anh}} = 3k_B \int_0^\infty (g_1(\varepsilon) - g_2(\varepsilon)) \ln(\varepsilon) d\varepsilon. \qquad (3)$$

Equation (3) is the classical limit of how the change in phonon DOS from temperature T_1 to T_2 provides an anharmonic contribution to the vibrational entropy of one phase. If the softening of the phonon DOS between temperatures T_1 and T_2 were different for two phases in a way to affect the integral in Eq. (3), the $\Delta S_{\text{vib}}^{\text{anh}}$ will differ for the two phases. This contributes to a difference in vibrational entropy between the two phases.

It is also true that Eq. (3) is the same expression for the difference in vibrational entropies of two phases, ''1'' and ''2,'' at the same temperature (the temperature of the phase transition, for example). We therefore used Eq. (3) for obtaining differences in vibrational entropies for all pairs of phonon DOS curves shown in Fig. 3. Using the phonon DOS at the lowest temperature (1073 K) as a reference, we present these results in Fig. 4. By extrapolating the temperature de-

pendencies of the phonon DOS of the $hP24$ and fcc phases to 1323 K, we obtain a change in vibrational entropy at the $hP24$–fcc phase transition temperature of $0.07k_B/$atom. This seems consistent with our previous result, obtained with temperatures further from the phase-transition temperature.[11] Since this entropy is an integral quantity, it is not influenced strongly by statistical errors in the measured data. Error bars from counting statistics and plausible variations of the data analysis procedure should be only $0.01k_B/$atom. For comparison, the configurational entropy of mixing of an alloy of A_3B composition is about $0.57k_B/$atom. The configurational entropy of the $hP24$–fcc phase transition is probably smaller than this, however, since we should expect some chemical short-range order in the fcc phase. Our diffraction data are inadequate for identifying short-range order, so we cannot quantify reliably the change in configurational entropy of the $hP24$–fcc transition. We expect, however, that the configurational entropy is several times larger than the vibrational entropy of the $hP24$–fcc phase transition.

It is interesting that the vibrational entropy of the $hP24$–fcc phase transition ($0.07k_B/$atom) is approximately equal to the entropy change caused by phonon softening over a temperature range of 100 K. These anharmonic phonon softenings are similar for both the $hP24$ and fcc phases, however, so there is a only a small anharmonic contribution to the thermodynamic preference of one phase over the other. The anharmonic effects on the vibrational entropy seem slightly larger for the $hP24$ phase, favoring this phase at higher temperatures. In addition to the thermal softening of the phonon DOS, we can estimate the anharmonic entropy using Eq. (1). Unfortunately, we do not have bulk moduli for the $hP24$ and fcc phases at high temperature, so we assume them to be equal and temperature independent. Using the result that the $hP24$ phase has a linear coefficient of thermal expansion at 1270 K that is 3% larger than that of the fcc phase at 1425 K, Eq. (1) predicts that the slope in Fig. 4 will be 6% larger for the $hP24$ than the fcc phase. The actual difference in Fig. 4 is approximately 15%. This discrepancy can be accounted for by the experimental errors in the linear coefficients of thermal expansion and uncertainties in the bulk moduli used in Eq. (1). We do not claim detailed agreement between our observed phonon softening and the classical predictions of Eq. (1) but the thermal softening of the phonon DOS is large enough to account for the classical thermodynamic behavior. Approximately, for an increase in temperature of 100 K, the thermal softening of the phonon DOS curves provides a vibrational entropy of the $hP24$ phase that increases by 0.01–$0.02k_B/$atom more than for the fcc phase.

The overall shapes of the phonon DOS curves do not undergo a qualitative change with temperature. We therefore attempted to describe the thermal softening of the phonon DOS curves with a Grüneisen approximation, where each phonon energy was rescaled,

$$\varepsilon \rightarrow \varepsilon (1 + 3\gamma\alpha\Delta T), \qquad (4)$$

and the phonon DOS was renormalized. Here ΔT is the difference in temperature of the two DOS curves. The Grün-
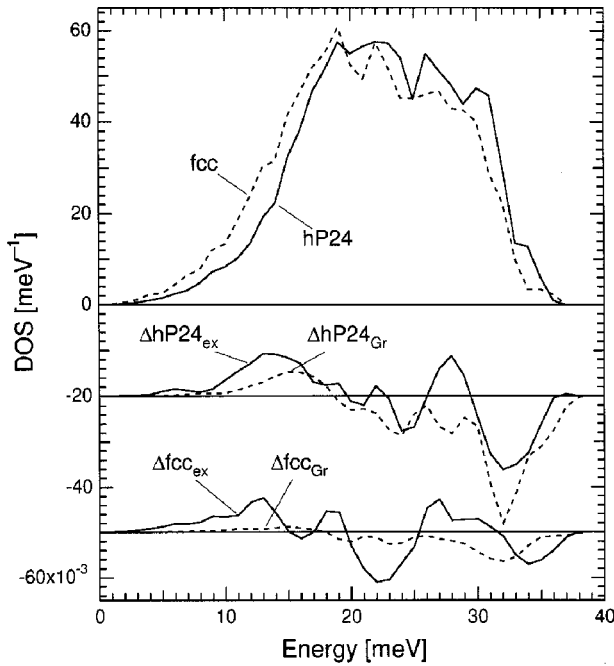
FIG. 5. Top: average of the phonon DOS curves of the fcc and $hP24$ phases. Bottom: ($\Delta hP24_{ex}$ and Δfcc_{ex}) are differences in the experimental phonon DOS curves between the pairs of DOS curves shown in Fig. 3(d) (for $hP24$ at 1308 and 1073 K), and Fig. 3(b) (for fcc at 1513 and 1333 K). ($\Delta hP24_{Gr}$ and Δfcc_{Gr}) are the differences, calculated using Eq. (5), between phonon DOS curves and the average DOS curves at the top of this figure.

eisen parameter γ was found by best fit between the DOS curves at the two temperatures to be 3.9 for the $hP24$ phase, and 1.7 for the fcc phase. These are average Grüneisen constants for all modes, so it is interesting to see if these constants pertain to individual features of the phonon DOS. When all phonon modes undergo the same thermal shift, the difference between two phonon DOS curves will be [Eq. (11) of Ref. 11, without typographical error]:

$$g_{T+\Delta T}(\varepsilon) - g_T(\varepsilon) = 3\gamma\alpha\Delta T\left(g_T(\varepsilon) + \frac{\partial g_T}{\partial\varepsilon}\varepsilon\right). \quad (5)$$

Figure 5 shows that this Grüneisen approximation of Eq. (5) makes poor predictions of the temperature dependencies of the phonon DOS curves of the $hP24$ and fcc phases. Both the calculated and experimental difference curves show peaks at the low energy part of the DOS curve and dips at higher energy, as expected from the phonon softening. Although the qualitative behavior may seem adequate for the $hP24$ phase, there is a large discrepancy in the predicted difference around 13 meV. The low-energy modes of the $hP24$ phase, probably dominated by low transverse-acoustic phonons, decrease more rapidly with temperature than predicted by the Grüneisen approximation. The prediction of the Grüneisen approximation is even worse for the fcc phase. The predicted difference at low energies is much too small, as is the difference at higher energies. An *ad hoc* increase in

the Grüneisen constant of the fcc phase to four or more leads to an overestimate of the difference at high energies, but a persistent underestimate at low energies. The differences in phonon DOS curves at two temperatures might be expected to be largest where the slopes are steepest. This occurs at about 13 and 32 meV. The problem with the Grüneisen approximation is that it predicts a shift in energy of an individual phonon in proportion to its energy, so the shifts at these two energies are predicted to be in the ratio of 32/13 = 2.5. Figure 3 shows, however, that the thermal softenings of the phonon DOS curves at these two energies are similar or perhaps even larger at 13 meV for the phonons of the $hP24$ phase.

V. CONCLUSIONS

Neutron-diffraction measurements on Co_3V at elevated temperatures showed that the low-temperature ordered $hP24$ phase ($P\bar{6}m2$) transforms to the fcc phase at 1323 K. The diffraction patterns of the $hP24$ phase showed no significant chemical disordering at temperatures approaching the $hP24$–fcc phase transition.

Phonon densities of states were obtained from inelastic neutron-scattering measurements on Co_3V at elevated temperatures. For comparison these DOS curves were measured at temperatures just across the $hP24$–fcc phase transition, and also at temperatures about 200° above and below the transition temperature. The vibrational entropy of the phase transition itself was $0.07k_B$/atom, with the fcc phase having the larger vibrational entropy. The configurational entropy of the $hP24$–fcc phase transition is expected to be several times larger. Over a temperature range of 100 K, the thermal phonon softening provides a change in vibrational entropy that is also about $0.07k_B$/atom. Nevertheless, the phonon softening is approximately the same for both the $hP24$ and fcc phases, leading to a small anharmonic contribution to the entropy difference between the $hP24$ and fcc phases. This difference seems to be slightly larger than $0.01k_B$/atom for a temperature increase of 100 K, with the $hP24$ phase having the larger anharmonic contribution. Within experimental uncertainties, these anharmonic contributions to the vibrational entropy seem consistent with the classical thermodynamic result expected from linear coefficients of thermal expansion of the two phases. Finally, since the thermal softening of the phonon DOS includes large changes at low energies (probably in the low transverse-acoustic modes), a simple Grüneisen approximation provides poor predictions of the thermal softening of the phonon DOS curves of both the fcc and $hP24$ phases.

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