



# Article Interdiffusion at Room Temperature in Cu-Ni(Fe) Nanolaminates

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**Abstract:** The decomposition of a one-dimensional composition wave in Cu-Ni(Fe) nanolaminate structures is quantified using X-ray diffraction to assess kinetics of the interdiffusion process for samples aged at room temperature for 30 years. Definitive evidence for growth to the composition modulation within the chemical spinodal is found through measurement of a negative interdiffusivity for each of sixteen different nanolaminate samples over a composition wavelength range of 2.1–10.6 nm. A diffusivity value  $\check{D}$  of  $1.77 \times 10^{-24} \text{ cm}^2 \cdot \text{s}^{-1}$  is determined for the Cu-Ni(Fe) alloy system, perhaps the first such measurement at a ratio of melt temperature to test temperature that is greater than 5. The anomalously high diffusivity value with respect to bulk diffusion is attributed to the nanolaminate structure that features paths for short-circuit diffusion through interlayer grain boundaries.

Keywords: nanolaminate; interdiffusion; spinodal; Cu-Ni(Fe)

## 1. Introduction

The process of spinodal decomposition [1-7] is a diffusional phase transformation. In this process, the growth of a periodic composition fluctuation spontaneously proceeds as an initial single-phase  $\alpha$ -matrix decomposes into separate  $\alpha'$  and  $\alpha''$  phases. The decomposition occurs without a change in the crystalline structure between the initial  $\alpha$  phase, and the final two  $\alpha'$  and  $\alpha''$  phases. This transformation occurs when the processing temperature and alloy composition are within the region of the phase diagram defined by the boundary called the chemical spinodal. The dynamics of nonlinear relaxation effects [8] are accounted for with respect to the interaction and motion of phase boundaries in a one-dimensional system.

The case for a nanolaminate, i.e., a nanoscale form of a multilayer structure, provides a onedimensional system in the form of an artificially synthesized, nanoscale composition fluctuation. Nanolaminates, functional multilayers, and their 2D unit materials are of general importance to fields such as improvements in fracture toughness for medical application [9], energy storage and battery anodes using electrochemical nanoarchitectonics [10,11], and magnetic materials with tunable in-plane anisotropy [12]. The relevance of interdiffusion in nanolaminates is of great importance regarding these applications as well as many others for assessing the robustness of structure in the context of maintaining performance over lifetime use.

The stability of an A/B nanolaminate composed of alternating A and B layers is modeled using the discrete theory [13] for a static concentration wave. The composition wavelength  $\lambda_{A/B}$  is the A/B layer pair thickness. The interdiffusivity coefficients are dependent on  $\lambda_{A/B}$  as a function of time at temperature  $T_i$ , as determined through the microscopic theory of diffusion [7,14–18]. The corresponding macroscopic diffusion coefficient  $\check{D}$  for the alloy system at  $T_i$  corresponds with an infinite composition wavelength, i.e., a wavenumber equal to zero. The interaction between interfaces is examined for prescribed composition fluctuations as determined by synthesis conditions. In this approach, parametric values for growth of the composition wave can be determined as arise from interfacial and gradient energy effects, including the critical wavenumber ( $\beta_{crit}$ ) above which growth occurs, and that wavenumber ( $\beta_{max}$ ) where the maximum amplification of growth is found for the decomposition process.

Diffusional interface motion can be modeled [14,19] with the use an analytic solution for the nonlinearity of decay in the composition profile through the use of higher-order interface interactions. The presence of lattice strains through the composition fluctuation introduces an additional effect [3,4] on the growth (or decay) of the composition fluctuation. The tendency towards an increase and even doubling of the composition wavelength as found [20] for  $Cu_{84}Ni_{10}Sn_6$  can occur for long time periods at elevated temperatures within the chemical spinodal. A recent Mössbauer study of a  $Cu_{79}Ni_{14}Fe_7$  alloy [21] aged at room temperature has shown spinodal decomposition. The growth (or decay) of the composition fluctuation is now examined for  $Cu_{53}$ -Ni<sub>40</sub>Fe<sub>7</sub> multilayer specimens that have been aged at room temperature for 30 years. The analysis method [19] recently improved [22] for quantifying higher-order gradient energy terms is again utilized for consistency with prior efforts to determine the interdiffusion kinetics of the one-dimensional, composition fluctuation.

#### 2. Materials and Methods

#### 2.1. Nanolaminate Synthesis and X-ray Characterization

The synthesis and X-ray diffraction characterization of the one-dimensional composition fluctuation to the Cu-Ni(Fe) nanolaminate superlattice structure are produced by physical vapor deposition. In brief, the Cu<sub>0.53</sub>-Ni<sub>0.40</sub>Fe<sub>0.07</sub> nanolaminates are synthesized [19,22] by alternating the vapor flux between Cu and a simultaneous exposure to Ni and Fe sources. In this study, the component A and B layers are of equal thickness to produce the characteristic A/B layer pair thickness, i.e., the composition wavelength ( $\lambda_{A/B}$ ). The deposition chamber is evacuated to a base pressure of 20 µPa (0.2 µTorr) with use of a liquid-nitrogen cooled Meissner trap. The source metals are >0.99995 pure and are thermally evaporated from 7 cm<sup>3</sup> crucibles at 0.1–1 nm·s<sup>-1</sup> evaporation rates to produce a 0.5–0.9 µm film thickness. The source-to-substrate separation of 30 cm enables thickness control with use of 6 MHz gold-coated quartz-crystal microbalances to produce a coating composition to within ±1 at.%. The nanolaminates coatings are deposited onto 4 cm × 8 cm sheets of both cleaved mica and polished Si wafers (with the native oxide intact). The substrate platen is oxygen-free Cu that is heated with a quartz lamp. A 20–40 nm thick buffer layer of pure Cu is deposited initially to introduce (111) film growth at a substrate temperature of 400 ± 10 °C. Deposition of the nanolaminate proceeds at a growth temperature of 350 ± 5 °C.

Since the initial synthesis and processing by thermal anneal treatments 30 years ago, X-ray diffraction scans are taken with a Rigaku Miniflex II diffractometer (Rigaku, Houston, TX, USA) operated in the  $\theta/2\theta$  mode using monochromatic Cu k $\alpha$  radiation as generated at 30 kV/20 mA using a graphite monochromator. Each  $\Delta 2\theta$  increment of rotation equals  $0.02^{\circ}$  with a 10 s dwell time. The integrated intensity of each peak reflection is computed from digitized X-ray reflectivity spectra using the de-convolution software provided with the Rigaku Miniflex II diffractometer. All X-ray intensity values are corrected [22] for composition-averaged atomic scattering ( $F_i$ ), Lorentz-polarization ( $L \cdot P$ ), mass absorption, and the Debye–Waller temperature effect on lattice vibration. The composition-averaged scattering and polarization terms is found [19,22] to dominate the intensity corrections for the Cu-Ni(Fe) samples. Detailed formulations of the diffraction analysis are provided in Appendix A.

#### 2.2. Analytic Interfdiffusion Model

Consideration of energetic effects account for changes in the composition fluctuation for growth within the spinodal, and the interaction between interfaces as formulated through higher-order gradient-energy terms in the modified diffusion equation. Detailed formulations of the modified

diffusion analysis are provided in Appendix B. The wavenumber  $\beta$  for the fluctuation is related to the composition wavelength  $\lambda$  as  $2\pi/\lambda$ . In accelerated processing times at higher isothermal anneal treatments, the wavenumber  $\beta_{max}$  with maximum amplification is seen [23] to decrease linearly with the cube-root of time  $t^{1/3}$  at various isothermal anneal temperatures. In addition, a strain energy effect is formulated [24] as the  $2\eta^2 Y$  term where the misfit strain between layer interfaces is  $\eta$  and the biaxial modulus is Y. Strain energy is known to inhibit growth of the composition fluctuation for associated wavelengths within the chemical spinodal producing a coherent spinodal regime, whereas diffusivity is enhanced due to strain energy at temperatures outside, i.e., above, the spinodal. A slowing effect over long-time periods towards a steady-state amplitude with an increased composition wavelength is modeled [15,16] within the spinodal that can account for nonlinear effects in the diffusivity behavior. Results obtained for quantifying the strain energy through modeling the effects on diffusion using fourth-order gradient energy terms evidence [22] these higher-order interface contributions to the spinodal decomposition of Cu-Ni(Fe) nanolaminates. The ln-scale change in the X-ray satellite intensity  $I^{\pm}(t)$  for the short-range ordering from the composition fluctuation as normalized to the Bragg peak intensity [22,25,26], is used to determine the amplification factor R. The shape of the amplification factor  $R(\beta)$  variation with its corresponding wavenumber  $\beta$  can change over long periods of time t. Herein, a dispersion relationship (B) is used to represent the wavenumber ( $\beta$ ) where the effects of crystalline orientation to the composition wave are accounted for quantitatively. The higher-order gradient-energy coefficients included in the expansion of the modified linear theory account for nonlinear effects of composition wavelength on diffusion and strain energy.

The interdiffusivity coefficients D(B) are derived from the measurement and behavior of the amplification factor R(B). The model for the gradient energy coefficients using the microscopic theory of diffusion is approached using a R(B) vs. B curve fit [22] rather than the  $\check{D}(B)$  vs.  $B^2$  curve [19]. The use of the R(B) vs. B curve is a more desirable analytic approach since the R(B) value will equal zero for the infinite-wavelength case when *B* equals zero, which then provides a unique boundary condition for the interpolative data analysis. This approach [22] provides a treatment of the data in a form closest to the experimental X-ray measurement where R(B) equals zero at B equals zero. For growth of the composition fluctuation within the spinodal, the simulated R(B) vs. B curve is fit to envelope all data as an upper bound [22], since strain energy accelerates [24] diffusion outside the spinodal but hinders it within. The  $\partial R/\partial B$  requirements guide the fitting procedure [22] to determine the order  $\mu$  of the polynomial to appropriately provide the correct (±) sign of the first  $k'_{\mu}$  term, where  $k'_1 < 0$  for decay and  $k'_1 > 0$  for growth. However, if the slope at B = 0 is negative, then the (±) signage would invert for  $K'_i$  and  $K_i$ . For case of  $k'_1 > 0$ , the result anticipated is  $K'_1 > 0$  and  $K_1 < 0$  since f'' < 0 and  $\check{D} < 0$  within the chemical spinodal. For decay at temperatures outside the spinodal, i.e.,  $T > T_s$ , use of the archival Cu-Ni(Fe) experimental data was evaluated to refine the computation [19,22] of the higher-order gradient energy coefficients  $K_{\mu}$ . The simulated model curve must again envelope all R(B) vs. B data since the presence of strain energy accelerates the diffusion process. In the D(B) vs.  $B^2$  variation for growth within the spinodal, a decrease in the absolute value of the wavenumber-dependent diffusion coefficient  $\check{D}(B)$  is found [22] where strain energy  $2\eta(B)^2 \Upsilon(B)$ effects are present. The effect of the operative diffusion mechanism on diffusivity behavior is evaluated for the Cu-Ni(Fe) nanolaminates aged at room temperature for 30 years. The analysis provides insight for the evaluation of the wavenumber-dependent strain-energy effect from growth or decay of the composition fluctuation.

## 3. Results

The changes observed to the original annealed condition of the as-deposited nanolaminates are quantified using analysis of the X-ray diffraction scans. The changes in the composition wave profile are determined using the diffuse scattering form the short-range ordering about the (111) Bragg reflection, that is representative of the long range order. The diffraction scans for nanolaminates with composition wavelengths of 3.05 and 3.19 nm are shown in Figure 1. The composition wavelength  $\lambda$  is

determined by the separation between the first-order satellite with the Bragg reflection. The effect of room temperature aging on the composition wavelength ( $\lambda$ ) of the nanolaminate is shown in Figure 2. The initial and final composition wavelength values are listed in Table 1. The slope of the dot-dash curve fit is 0.978 in Figure 2, with a correlation coefficient of 0.972. There is no significant change (i.e., <2%) in composition wavelength. However, a shift towards a 3-nm final spacing is found for initial wavelengths between 2 and 4 nm.



**Figure 1.** The  $\theta/2\theta$  X-ray diffraction scans shows the satellite peaks below (-1) the (111) Bragg reflections of the Cu-Ni(Fe) nanolaminates with composition wavelengths of 3.04 nm (green curve) and 3.15 nm (blue curve) and the (Cu) base layer for epitaxial growth.



**Figure 2.** The final wavelength of the composition modulation after long-term aging is plotted as a function of the initial (as-deposited) wavelength for each Cu-Ni(Fe) nanolaminate.

The amplification factor (R) for each nanolaminate is computed from the normalized, integrated intensity values and the 2 $\theta$  position of each diffraction peak. The ratio between the normalized satellite and Bragg peaks is compared between the as-deposited condition, and after 30 years aging at room temperature. An initial nonlinear response [19,22] in the ln-scale, normalized-satellite intensity variation with anneal time, i.e., amplification factor R, that can occur from a strong composition

dependence in Cu-Ni [27,28] is not anticipated in this study since the growth of the composition fluctuation at room temperature is measured using nanolaminates that had initially undergone significant homogenization [19] at temperatures outside the spinodal to greatly reduce the amplitude of the composition profile to a small fluctuation—a necessary condition for the diffusion model.

Wavelength $\lambda$ (nm)		$B^2$	$(I_{-1}/I_{\rm B})_{\rm corrected}$		<i>R</i> ( <i>B</i> )	Ď(B)
Initial	Final	(nm <sup>-2</sup> )	Initial	Final	$(10^{-10} \text{ s}^{-1})$	$(10^{-24} \text{ cm}^2 \cdot \text{s}^{-1})$
10.63	10.51	0.35	0.17590	0.18879	0.37	-1.037
8.61	8.54	0.54	0.11493	0.13803	0.94	-1.746
6.46	6.40	0.95	0.06798	0.10785	2.44	-2.563
6.16	6.17	1.04	0.03480	0.07060	3.74	-3.612
5.55	5.61	1.26	0.03427	0.07445	4.10	-3.248
4.34	4.11	2.20	0.01351	0.04003	5.82	-2.648
4.24	3.32	2.43	0.00344	0.00627	3.20	-1.314
4.24	3.37	2.70	0.00959	0.02561	5.19	-1.919
3.68	3.80	2.80	0.00286	0.01136	7.24	-2.588
2.58	3.05	4.91	0.00539	0.01349	4.86	-0.991
2.41	3.19	4.95	0.00413	0.00890	4.05	-0.818
2.22	2.01	8.16	0.00331	0.00955	5.65	-0.692
2.16	2.23	7.97	0.00302	0.00851	5.54	-0.695
2.14	2.19	8.17	0.00156	0.00383	4.71	-0.576
2.10	2.05	8.77	0.00126	0.00221	2.99	-0.341
2.07	2.07	8.90	0.00539	0.00654	1.00	-0.112

Table 1. X-ray diffraction and diffusivity measurements of Cu-Ni(Fe) at 23 °C.

The variation of the amplification factor *R* with the dispersion relation *B* of the Cu-Ni(Fe) structure is plotted in Figure 3. The corresponding  $B^2$  values from the dispersion relation used for each nanolaminate in the Figure 3 plot are listed in Table 1 along with the *R*-value computed from the X-ray diffraction measurements and the corresponding value computed for the interdiffusivity  $\check{D}(B)$ . The Table 1 list for the corrected integrated intensity value of the first order satellite reflection below the Bragg peak is the  $(I_{-1}/I_B)$  corrected value. Two sets of curves are fit to the data points plotted in Figure 3.



**Figure 3.** The amplification factor R (10<sup>-10</sup> s<sup>-1</sup>) that is computed for Cu-Ni(Fe) from changes in the X-ray diffraction profile is plotted as a function of the dispersion relation B (nm<sup>-1</sup>) wavenumber.

Curve 1 considers the variation of *R* as a function of *B* with a single peak value at  $2.2 \text{ nm}^{-1}$  for the maximum amplification factor—corresponding to the composition wavelength of maximum growth.

In the case for maximum growth, the enveloping simulated curve fit  $R_s$  in Figure 3 has a large difference compared to the experimental values of  $R_e$ . Curve 2 uses a higher-order polynomial fit to envelope the distribution of points to minimize the difference with the experimental R values. Curve 2 features a bimodal peak for the amplification factor R with respect to the dispersion relation B. The bimodal distribution of Curve 2 can be considered the superposition of two constituent curves as, e.g., Curves 2a and 2b—each with a peak value for maximum amplification of growth that appear at 1.7 and 2.9 nm<sup>-1</sup>, respectively. The curves for the R versus B variation of Figure 3 are next used to compute the curve simulations that fit the data points plotted in Figure 4 for the variation of  $\check{D}(B)$  as a function of  $B^2$ .

The  $\tilde{D}(B)$  values of each data point are plotted in Figure 4 as listed in Table 1. The accuracy in determining the interdiffusivity coefficients is indicated with error bars in Figure 4. The error in  $\tilde{D}(B)$  can reaches a maximum of 35% for a few individual samples with a  $B^2$  value near 2 nm<sup>-2</sup>. The Curve 1 fit in Figure 4 for the  $\tilde{D}(B)$  data is nearly a straight line as would be in accordance with a singular, first-order gradient energy coefficient. A significant deficiency of the Curve 1 fit is that the decrease in  $\tilde{D}(B)$  values that trend below a  $B^2$  value of 1 nm<sup>-1</sup> cannot be reproduced as observed in the experimental data using a first order curve, nor would a third order curve accommodate the additional inflection towards as  $\tilde{D}(B)$  approaches a value of zero at  $B^2 = 0$ . Curve 2 is seen to appropriately envelope the diffusivity values, thereby minimizing the Fourier energy component. The accuracy of the interdiffusivity intercept value  $\tilde{D}$ , i.e.,  $\tilde{D}(B)$  at  $B^2 = 0$ , is uncertain as the constituent 2a and 2b curves produce  $\tilde{D}(B)$  values >0 and <0, respectively. The higher-order gradient energy coefficients that are fit to the Figure 4 curves are listed in Table 2, along with the corresponding computed values for the interdiffusivity intercept value  $\tilde{D}$  ( $10^{-10}$  nm<sup>2</sup>·s<sup>-1</sup>), mobility M ( $10^{10}$  nm<sup>2</sup>·J<sup>-1</sup>·s<sup>-1</sup>), and second derivative f'' ( $10^{-18}$  J·nm<sup>-3</sup>) of the Helmholtz free energy per atom volume.



**Figure 4.** The interdiffusivity  $\check{D}(B)$  ( $10^{-24}$  cm<sup>2</sup>·s<sup>-1</sup>) is plotted as a function of the dispersion relationship  $B^2$  (nm<sup>-2</sup>) for Cu-Ni(Fe) as computed using Figure 3 amplification values R(B) (s<sup>-1</sup>).

The Curve 1 fit in Figure 4 for the D(B) data is nearly a straight line as would be in accordance with a singular, first-order gradient energy coefficient. A significant deficiency of the Curve 1 fit is that the decrease in D(B) values that trend below a  $B^2$  value of 1 nm<sup>-1</sup> cannot be reproduced as observed in the experimental data using a first order curve. Also, a third order curve will not accommodate the additional inflection towards as  $\check{D}(B)$  approaches a value of zero at  $B^2 = 0$ . Curve 2 is seen to appropriately envelope the diffusivity values, thereby minimizing the Fourier energy component. The accuracy of the interdiffusivity intercept value  $\check{D}$ , i.e.,  $\check{D}(B)$  at  $B^2 = 0$ , is uncertain as the constituent 2a and 2b curves produce  $\check{D}(B)$  values >0 and <0, respectively. The higher-order gradient energy coefficients that are fit to the Figure 4 curves are listed in Table 2, along with the corresponding computed values for the interdiffusivity intercept value  $\check{D}$  (10<sup>-10</sup> nm<sup>2</sup>·s<sup>-1</sup>), mobility M  $(10^{10} \text{ nm}^2 \cdot \text{J}^{-1} \cdot \text{s}^{-1})$ , and second derivative f''  $(10^{-18} \text{ J} \cdot \text{nm}^{-3})$  of the Helmholtz free energy per atom volume. The D values are the D(B) axis intercepts for Curves 1 and 2 in Figure 4. The values for Dare on the order of  $(-1 \pm 0.3) \times 10^{-10} \text{ nm}^2 \cdot \text{s}^{-1}$ , as listed in Table 2. The accuracy in determining the diffusivity coefficients for these curves 2 and 1 at  $B^2 = 0$  is limited by a total error of 30–35%, respectively. This error is orders of magnitude greater than the D value of  $-1 \times 10^{-26}$  nm<sup>2</sup>·s<sup>-1</sup> at 23 °C which could be extrapolated [22] from high-temperature data for Ni<sup>63</sup> self-diffusion [29] where  $\check{D}(T)$  at  $T^{-1} = 0$  equals  $\check{D}_0 \sim 1 \text{ cm}^2 \cdot \text{s}^{-1}$ . To reconcile this difference, the third data-point fit is considered where the  $\check{D}$  value of  $-1 \times 10^{-26}$  nm<sup>2</sup>·s<sup>-1</sup> at 23 °C is assumed, and the required values of the gradient energy coefficients are computed (as listed in Table 2) along with the required order of magnitude for the amplification factor R. In this third fit, it's found that the gradient energy coefficients would have to be 10-12 orders of magnitude smaller than measured, and that the corresponding *R* values would need to be 16 orders of magnitude smaller than actually measured. The variation of the Fourier energy term  $(F_e/f'')$  with composition wavelength is plotted in Figure 5.



**Figure 5.** The variation of the Fourier energy term ( $F_e/f''$ ) with composition wavelength  $\lambda$  (nm) is computed from the interdiffusivity data for the Cu-Ni(Fe) nanolaminates at 23 °C.

Table 2. Computed diffusivity and gradient energy coefficients for Cu-Ni(Fe) at 23 °C.

Curve Fit	1	2	2a	2b	3
$\check{D}$ (10 <sup>-10</sup> nm <sup>2</sup> ·s <sup>-1</sup> )	-4.108	-1.767	0.7208	-0.9222	$-1.00 imes10^{-16}$
$M (10^{10} \text{ nm}^2 \cdot \text{J}^{-1} \cdot \text{s}^{-1})$	2.383	1.025	-41.82	53.51	$5.80 imes10^{-17}$
$f'' (10^{-18} \text{ J} \cdot \text{nm}^{-3})$	-1.484	-1.484	-1.484	-1.484	-1.484
$K_1 (10^{-20} \mathrm{J} \cdot \mathrm{nm}^{-1})$	8.683	-140.2	244.2	-204.1	$-1.93  imes 10^{-10}$
K <sub>2</sub> (10 <sup>−21</sup> J·nm)	-2.438	711.3	-1166	866.9	$1.30 imes10^{-11}$
$K_3 (10^{-22} \text{ J} \cdot \text{nm}^3)$	1.264	-1106	1945	-1142	$-2.35  imes 10^{-12}$
$K_4 \ (10^{-23} \text{ J} \cdot \text{nm}^5)$	-	554.3	_	506.8	$1.36  imes 10^{-11}$

The computation of  $F_e/f''$  in Figure 5 is made using the value of  $\Delta D(B)$  that corresponds to the difference between the Curve 2 fit and the interdiffusivity data of Figure 4 where  $F_e(h)$ equals  $\Delta D(B) \cdot [f'(h)/D]$ . The values of  $F_e/f''$  as plotted in Figure 5 are comparable to those found previously [18] for computations at higher temperatures, specifically outside the spinodal at 345 and 400 °C, as well as within the spinodal at 320 °C. The local maximum in the  $F_e/f''$  curve occurs at a composition wavelength consistent with the local maximum in absolute value of the interdiffusivity D(B) coefficient as plotted in Figure 4. Note, the corresponding values of  $F_e/f''$  would have to be 16 orders of magnitude greater (than those shown in Figure 5) for the third data fit requirement of Table 2. So, a D value of  $-1 \times 10^{-26}$  nm<sup>2</sup>·s<sup>-1</sup> that would correspond with bulk diffusivity does not appear to be a feasible consideration for the Cu-NiFe room temperature data. The Curve 1 fit of Table 2 would produce a comparable curve as shown in Figure 5, but scaled to a maximum value of  $F_e/f''$ equal to just 0.40 at a composition wavelength of 4.0 nm.

#### 4. Discussion

The use of a bimodal curve to model the amplification factor of Figure 3 reproduces the experimental variation of interdiffusivity in Figure 4. In addition, the diffusivity D values that are determined from the model curves of Figures 3 and 4 as listed in Table 2 appear anomalously high in comparison to the bulk diffusivity at room temperature. Considerations are offered for additional mechanisms responsible for the observed diffusion behavior.

#### 4.1. Bimodal Interdiffusion Behavior

The wavenumber  $\beta_{max}$  for the maximum amplification of the composition wave should decrease with time as attributed to nonlinear diffusion as independent of strain energy. However, the suppression of the coherent spinodal for long wavenumbers with strain energy contributions will tend to shift the critical wavenumber  $\beta_{crit}$  for allowable growth to greater values since the driving force of the Helmholz free energy increases proportional to the decrease in the process temperature below the chemical spinodal. Consequently, the change in  $\beta_{crit}$  would tend to shift the maximum amplification to a larger wavenumber  $\beta_{max}$ , although with slower kinetics.

The presence of strain energy can be found in (some but not all) nanolaminate alloy samples. The corresponding coherent spinodal temperature  $T_s^*$  for growth will be suppressed to lower values below the chemical spinodal  $T_s$ . This attribute of strain energy will, again, slow the growth of samples with larger wavenumbers since coherency effects result from epitaxial growth. In general, the strain energy effect increases for thinner epitaxial and coherent layers of the one-dimensional artificial fluctuation, hence shorter interface separations. Coincident with the state of coherency, is the effect of strain and crystalline orientation on the biaxial modulus  $Y(\eta)$ . In general, tensile strains and non-close packed directions tend to soften the modulus. If the modulus softens, then the  $2\eta^2 Y$  barrier that inhibits diffusion will be lowered. Consequently, an increase would be found in the coherent spinodal temperature  $T_s^*$ .

Competing effects are now found in the trends that shift the wavenumbers preferred for maximum growth of the composition wave at room temperature. First, nonlinear diffusion effects will shift maximum growth to shorter wavenumbers, i.e., longer wavelengths. Second, strain energy slows the growth of specimens affected wherever interface strain is present. This interface-induced strain effect is more pronounced at longer wavenumbers, i.e., shorter wavelengths. The maximum amplification for growth can shift to short wavenumbers with the further decrease of temperature below the chemical spinodal—where samples with longer wavenumbers can preferentially grow. Thus, the further the temperature is decreased below the chemical spinodal, we can expect the shape of the R(B) versus B curve to change as a consequence of the  $\beta$ -dependence of strain energy. Since the  $2\eta(B)^2 Y(\eta)$  term is not constant, a change can be seen in the classic relationship between  $\beta_{max}$  and  $\beta_{crit}$ . A transition to a bimodal shape of the R(B) versus B curves occurs when comparing results for temperatures just

below the chemical spinodal  $T_s$  to temperatures well below the coherent spinodal  $T_s^*$  where  $\beta_c$  may no longer equal  $\beta_m \cdot \sqrt{2}$ . A shift to an amplified growth should be seen towards shorter wavenumbers as a consequence of nonlinear diffusion, whereas growth can be expected at disproportionately longer wavenumbers due to an increased Helmholz free energy. The result seen in the data plots of Figures 3 and 4 is a bimodal distribution in R(B) versus B curve as the outcome of room temperature aging. A decrease in wavenumber  $\beta$ , and corresponding increase in  $\lambda$  for maximum growth is seen from a value of 1.8 nm reported [22] at 320 °C to a 3.7 nm at room temperature as found in Figure 3 and listed in Table 1.

#### 4.2. Anomalous Diffusivity

The extrapolation of high-temperature bulk-diffusivity data for Cu-Ni(Fe) [30–32] and other alloys to low temperatures is made in Figure 6 using the Arrhenius relationship between D and  $T^{-1}$  as normalized to the melt temperature  $T_m$  of the matrix metal alloy. The bulk diffusion mechanism requires consideration of atomic diffusion through the lattice, as e.g., via vacancies and interstitials. The bulk diffusivity that would result at room temperature is well below by 16 orders of magnitude—the anomalously high diffusivity determined for the Cu-Ni(Fe) nanolaminates. As such, additional mechanisms for diffusion are now considered that are much faster than found in the bulk at lower temperatures. For example, a transition in diffusion behavior can be observed below half the melt point where a much faster rate of nano-micro-polycrystalline grain growth occurs [33,34] than would correspond to bulk diffusion. The higher diffusion rates become prevalent, often, though the transport of atoms along paths that short circuit [35,36] the bulk diffusion process. Alternative paths for progressively higher diffusivities can be found along dislocation-pipes, grain boundaries, and surfaces. The grain boundaries between layers in nanocrystalline nanolaminate materials provides such features as needed for enhanced diffusion.

The diffusion coefficients associated with each type of mechanism [35] are shown in the Arrhenius plot of Figure 6 where the linear curves progress with an increasing value of the diffusion coefficient from (lattice or) bulk-, to (dissociated) dislocation-, to (undissociated dislocation) grain boundary-diffusion. Vacancy migration is most restricted by the lattice in bulk diffusion—much less so due to high vacancy concentrations in the distorted structure of dislocation cores; and even less in grain boundaries along secondary dislocation cores similar [36] to undissociated dislocation cores that are present in low-angle grain boundaries. Here, enhanced diffusion can occur along zig-zag paths for partials with extended and constricted nodes. High diffusivities are found for semiconductor interfaces at lower temperatures as well. A high atomic mobility of Si and Ge at (Si,Ge)-Al interfaces is reported [37] at only 80 K. Similarly, the diffusion of Hf at 950 °C is reported [38] along linear defects in HfN-ScN nanolaminate; for Cu diffusion at 450 °C [39] along internal interfaces in Cu-AlN nanolaminates; and for Si-Al [40] as well. In these high-temperature studies, high-resolution electron microscopy (HREM) and atom probe methods are used for measuring the effect of solute concentration due to atomic diffusion along dislocations and grain grain boundaries. However, there are inherent limitations in the structure of the Cu-Ni(Fe) nanolaminates of this study where the effects of layer curvature and tapered nanocrystalline grains adversely affect the resolution of grain boundaries, and the ability to distinguish boundary composition from the grain interior. Thus, the experimental method employed, i.e., that of X-ray diffraction, provides the method of assessing the kinetics of atomic transport during the diffusion process.

The effect of dislocations on diffusion kinetics in solids can be categorized as well by three basic types [41] of length scale where type-A refers to long diffusion distances, type-B refers to higher temperatures and longer anneal times with a diffusion distance on the order of the scale of the dislocation network, and type-C to lower temperature and shorter times where it can be considered that the diffusion is taking place only in the dislocation network itself. Type-C is considered that for grain boundary diffusion. <sup>63</sup>Ni isotope diffusion with type-C behavior is measured in: polycrystalline Cu [42] over the temperature range of 476–635 K; nanocrystalline Cu [43] with 35–55 nm grain sizes

over 420–470 K; and pure Cu subjected [44] to surface mechanical attrition treatment (SMAT) over 293–438 K. Diffusion coefficients from these studies are plotted in Figure 6 indicating that the  $^{63}$ Ni in Cu data rests on the guideline for grain boundary diffusion. <sup>59</sup>Fe isotope diffusion in Cu [45] is measured in the temperature range of 529–758 K. Corresponding diffusion coefficient data plotted in Figure 6 shows that the <sup>59</sup>Fe in Cu diffusion data rests just above the dislocation diffusion guideline. Similarly, <sup>59</sup>Fe in diffusion in pure Cu and CuFe alloys under type-B conditions [46], indicates diffusion occurs along grain boundaries with leakage into the grain bulk. The effect of impurity on grain boundary self-diffusion of the <sup>63</sup>Ni isotope in polycrystalline Ni [47] indicates diffusion decreases with increasing impurity. These type-C diffusion results in the 584–640 K range are plotted in Figure 6 for 0.99999 pure Ni. The <sup>63</sup>Ni self-diffusion in Ni data rests just below the grain boundary diffusion guideline. The present room-temperature Cu-Ni(Fe) result is the data point marked by the largest (solid red) circle in Figure 6. The diffusion coefficient computed at 23 °C rests just below the guideline for grain-boundary diffusion mechanism, and may well represents an extension of the grain-boundary diffusion data [38-43] for both Ni and Fe in Cu as well as Ni self-diffusion. The lack of grain growth, i.e., recrystallization, implies that the role of grain-boundary motion induced diffusion [48] is not a significant factor for the nanolaminates of this study whereas the use of grain boundaries and dislocation pipes provide paths for accelerated atomic transport between layers.



**Figure 6.** The Arrhenius plot of experimental diffusivity  $\check{D}$  (cm<sup>2</sup>·s<sup>-1</sup>) data with the ratio of melt point  $T_{\rm m}$  to test temperature T for the Cu-Ni(Fe), Ni-Cu, Fe-Cu, Ni-Ni, Si-Al, and HfN-ScN systems is shown along with generic diffusivity curves [32] for identifying the bulk-, dislocation-, and grain boundary-based diffusion mechanisms ( $\diamond$  Jankowski [22];  $\blacktriangle$  Gust, et al. [30];  $\blacksquare$  Poerschke, et al. [31,32]; • Tsakalakos and Hilliard [16];  $\blacktriangle$  Garbrecht, et al. [38];  $\diamond$  Legros, et al. [40];  $\blacksquare$  Divinski, et al. [42];  $\bigstar$  Wegner, et al. [43];  $\blacksquare$  Ribbe, et al. [45]; • Prokoshkina, et al. [47]; • Wang, et al. [44]; • present).

The most pronounced effect of enhanced diffusivity at room temperature is seen in Table 1 for the nanolaminates with a 6.1 nm layer pair spacing. At longer (and shorter) wavelengths of the nanolaminate, the  $\check{D}(B)$  value decreases. A possible cause is that the enhanced diffusion from the grain boundary mechanism diminishes as the boundary length between interfaces becomes too long (or is inhibited by strain energy effects that often predominate at shorter wavelengths). This room temperature aging study accentuates the competitive effects from diffusion along grain boundaries as introduced by a nanocrystalline grain size. The stability of nanocrystalline nanolaminates at lower temperatures should be considered with respect to the interplay between dominate diffusion mechanism as influenced by grain size, hence grain boundary effects.

#### 5. Conclusions

The process of spinodal decomposition in Cu-Ni(Fe) is assessed using a one-dimensional composition fluctuation in nanolaminate structures consisting of alternating Cu and Ni(Fe) layers. The diffusivity is determined for an aging period of 30 years at room temperature. X-ray diffraction is used to measure satellite-peak intensities that correspond with changes in the short-range order, which indicates change to the one-dimensional composition fluctuation of the nanolaminate structure. There is definitive evidence for growth to the composition modulation within the spinodal as measured by a negative interdiffusivity for each of the nanolaminate samples. The competing effects of time, and suppression in temperature below the chemical spinodal for a strain layered structure produce an apparent bimodal distribution of the amplification factor R with wavenumber  $\beta$ . A contributing factor to this behavior is the dependence of strain energy within the nanolaminate structure that is on the order of  $1 \times 10^{-18}$  J·nm<sup>-3</sup> and which is dependent upon the composition wavelength. An upper-bound in interdiffusivity  $\check{D}(B)$  is observed that peaks at  $(3.6 \pm 1.1) \times 10^{-24} \text{ cm}^2 \text{ s}^{-1}$  for a composition wavelength  $\lambda$  of 6.2 nm, and then decreases rapidly with increasing wavelength as the oriented corrected wavenumber  $\beta$  approaches zero. Overall, the diffusivity  $\check{D}$  of (1.8  $\pm$  0.5)  $\times$ 10<sup>-24</sup> cm<sup>2</sup>·s<sup>-1</sup> is anomalously high for the Cu-Ni(Fe) alloy system with respect to bulk diffusion and can be attributed, perhaps, to diffusion mechanism(s) consistent with transport along dislocation pipes and grain boundaries. The novelty in the three-decade time lapse for this study of diffusion kinetics is that the measurements are made at room temperature, i.e., perhaps the first measurement at a ratio of melt temperature to test temperature that is greater than 5, and where spinodal decomposition is observed in a metal alloy system at a diffusivity of only  $10^{-24}$  cm<sup>2</sup>·s<sup>-1</sup>.

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### Appendix A

Integrated intensity values  $I_c$  are corrected from measured  $I_m$  values [22,26] through consideration of effects as composition-averaged scattering, polarization, mass absorption and temperature according to the following expression.

$$I_{\rm c} = (I_{\rm m})/(F^2 \cdot L \cdot P \cdot T_x \cdot D_w) \tag{A1}$$

The  $I_m$  intensities are normalized with respect to the following factors: *F*—For the compositionaveraged atomic scatterings  $F_i$ ;  $L \cdot P$ —The Lorentz polarization effect as corrected for a graphite monochromator that, in this case, is found at a Bragg angle  $2\alpha$  of  $25^\circ$ ;  $T_x$ —For the product of the mass absorption coefficient  $\mu/\rho$  with density  $\rho$  and specimen film thickness x; and  $D_w$ —The Debye-Waller temperature effect on lattice vibration. The product of  $F^2 \cdot L \cdot P$  is the dominant term in Equation (A1). The Cu-Ni(Fe) nanolaminate is treated as a pseudobinary alloy with respect to composition  $c_i$  consisting of Cu and Ni(Fe) layers. The parametric components of Equation (A1) are provided as follows where he magnitude of displacement for the scattering vector  $\hat{u}$  is used in Equations (A2a)–(A2k).

$$F = c_{\mathrm{Cu}} \cdot F_{\mathrm{Cu}} + c_{\mathrm{NiFe}} \cdot F_{\mathrm{NiFe}} = c_{\mathrm{Cu}} \cdot F_{\mathrm{Cu}} + (1 - c_{\mathrm{Cu}}) \cdot F_{\mathrm{NiFe}}$$
(A2a)

$$F_{\rm Cu} = 18.9 - 3.3 \cdot [\sin(\theta) / \lambda_{\rm X-ray} - 2]$$
 (A2b)

$$F_{\rm Ni} = 20.7 - 3.5 \cdot [\sin(\theta) / \lambda_{\rm X-ray} - 2]$$
(A2c)

$$F_{\rm Fe} = 21.6 - 3.7 \cdot [\sin(\theta) / \lambda_{\rm X-ray} - 2]$$
(A2d)

$$F_{\rm NiFe} = c \cdot F_{\rm Fe} + (1 - c) \cdot F_{\rm Ni} \tag{A2e}$$

$$c = c_{\rm Fe} / (c_{\rm Fe} + c_{\rm Ni}) \tag{A2f}$$

$$L \cdot P = \left[1 + \cos^2(2\alpha) \cdot \cos^2(2\theta)\right] / \left\{\left[1 + \cos^2(2\alpha)\right] \cdot \left[\sin^2(\theta) \cdot \cos(\theta)\right]\right\}$$
(A2g)

$$T_{\rm x} = 1 - e[-2\mu \cdot x/\sin(\theta)] \tag{A2h}$$

$$D_{\rm w} = \mathbf{e}[-2\underline{B}\cdot H] \tag{A2i}$$

$$H = [\sin(\theta)/\lambda_{X-ray}]^2$$
(A2j)

$$\underline{B} = (2\pi \cdot \hat{\mathbf{u}})^2 \tag{A2k}$$

## Appendix B

A review of the modified diffusion formulation [22,26] for the stability of a nanolaminate interface with respect to diffusion along the composition fluctuation is provided as follows. The composition wavelength, i.e., layer pair spacing,  $\lambda_{A/B}$  of the fluctuation between A-rich and B-rich regions is equated to the wavenumber  $\beta$  as  $2\pi/\lambda_{A/B}$ . A schematic of the A/B nanolaminate structure is shown in Figure A1. The A-rich layers have some amount of element B, i.e., labeled A(B), as the interdiffusion process progresses, and B-rich layers have some amount of element A, i.e., labeled B(A). Dashed lines are used to show the nominal interface (i) between the layers, a dislocation (d) in the B(A) layer, and a grain boundary (gb). A transmission electron microscopy study [49] reveals the ultra-fine grain nanocrystalline structure to the nanolaminate as seen in the bright field image and selected-area diffraction pattern (SADP) of a 4.34 nm layer pair Cu-Ni(Fe) as viewed in-plane. The SADP is indexed to {111} with features of twinning and in-plane grain rotation.



**Figure A1.** The A/B nanolaminate structure with A (dark-shaded atoms) and B (light-shaded atoms) is viewed (**a**) in cross-section, and a plan view image (**b**) with a selected-area diffraction pattern (insert) of the 4.34 nm Cu-Ni(Fe) nanolaminate reveals its ultra-fine grain nanocrystalline structure.

The microscopic theory of diffusion quantifies the interdiffusivity coefficient  $D_B$  of each nanolaminate as dependent upon  $\lambda_{A/B}$  at temperature  $T_i$ . The relative decay in satellite intensity  $I^{\pm}(t)$  with time *t* for the composition fluctuation is normalized to the Bragg peak intensity as described in Appendix A, and this corrected-intensity value is used to determine the amplification factor *R* as follows.

$$\ln\{[I^{\pm}(t)]/[I^{\pm}(0)]\} = 2R \cdot t \tag{A3}$$

The amplification factor *R* is related to the generalized  $D_B$  through the dispersion relationship  $B^2(\beta)$  according to the following expression.

$$R = -B^2(\beta) \cdot \check{D}_B \tag{A4}$$

The  $B^2(h)$  expression for face-centered-cubic [100] or [111] growth is seen in the following relationship.

$$B^{2}(h) = 2\{1 - \cos(2\pi h)\} / d_{(hkl)}^{2}$$
(A5)

The interplanar spacing is  $d_{(hkl)}$ , and h is equal to  $d_{(hkl)}/\lambda_{A/B}$ . The use of a curvilinear fit to the variation of  $\check{D}_B$  with  $B^2(h)$  yields the value at  $B^2(h) = 0$  of the macroscopic diffusion coefficient, i.e., diffusivity  $\check{D}$ . That is, a nanolaminate with an infinite composition wavelength is the equivalent of a macroscopic diffusion couple. A generalized expression for  $\check{D}_B$  is presented in terms of its energetic components to account for potential nonlinear effects. The  $\check{D}$  coefficient is related to  $\check{D}_B$  through the Fourier transform  $F_e(h)$  of the elastic strain energy for the distorted lattice, the second derivative f'' of the Helmholtz free energy (per atom volume  $N_v$ ), and the gradient-energy coefficients  $K_{\mu}$  as follows.

$$\check{D}_{B} = \check{D} \cdot \{1 + F_{e}(h) / f'' + (2/f'') \cdot \Sigma[K_{\mu} \cdot B^{2\mu}(h)]\}$$
(A6)

For a face-center cubic system,  $N_v$  equals  $4/a^3$  for an alloy lattice parameter *a*. The order of the polynomial is  $\mu$ , and the diffusion coefficient  $\check{D}$  is related to the mobility *M* according to the following expression.

$$\check{D} = (M/N_{\rm v}) \cdot f'' \tag{A7}$$

The f'' and  $K_{\mu}$  terms in Equation (A6) are identical with expressions that appear in both the continuous and discrete theories of spinodal decomposition. The expression for the diffusion coefficient used in Equation (A7) includes only the Helmholtz free energy term f'' because the presence of strain energy is not a prerequisite, but it varies with each nanolaminate sample. A direct series expansion of the  $\check{D}_B$  with  $B^2(h)$  relationship is now used to fit the experimental intensitydata, using Equations (A1), (A3) and (A4) as follows.

$$\check{D}_B = \check{D} \cdot [1 + \Sigma K'_{\mu} \cdot B^{2\mu}(h)] \tag{A8}$$

Accordingly, from Equations (A7) and (A8), the coefficients  $K'_{\mu}$  are used to compute the gradient energy coefficients  $K_{\mu}$ , where  $K'_{\mu}$  is now equal to  $2K_{\mu}/f''$ . The  $F_{e}(h)$  quantity is equated with strain energy and is, therefore, a function of B(h). The strain energy term equals  $2\eta^2 \cdot Y$ , where  $\eta$ is the compositionally dependent variation of strain that equals  $(1/a) \cdot (\partial a / \partial c)$ , and Y is the  $\langle hkl \rangle$ orientation-dependent biaxial modulus. The diffusivity equals zero at the coherent spinodal ( $T_s^*$ ). From the linear theory using Equation (A6) where only one gradient energy coefficient is considered, the following condition is found.

$$f'' + 2\eta^2 \cdot Y + 2K \cdot B^2 = 0$$
 (A9)

The gradient energy coefficient *K* can be determined from Equation (A9) with respect to the critical wavenumber where there is no growth or decay. Where the wavenumber *B* equals zero, i.e., for a macroscopic diffusion couple where the wavelength goes to infinity, Equation (A9) reduces to

$$f'' + 2\eta^2 \cdot Y = 0 \tag{A10}$$

This relationship indicates that the f'' = 0 condition for the chemical spinodal is changed with a suppression to the condition of  $f'' = -2\eta^2 \cdot Y$  for the coherent spinodal. From an experimental estimate of the chemical spinodal temperature  $T_s$ , the value of f'' for any temperature can then be computed using Boltzmann's constant  $k_B$  as

$$f'' = N_{\rm v} \cdot k_{\rm B} \cdot (T - T_{\rm s}) / [c \cdot (1 - c)]$$
(A11)

The amount that the coherent spinodal temperature is suppressed below the chemical spinodal, i.e.,  $T_s - T_s^*$ , can be determined using Equation (A10) where the temperature *T* is now equated as  $T_s^*$ .

Growth of the composition fluctuation when  $T < T_s$  requires that the diffusivity is negative ( $\check{D}_B < 0$ ) for uphill diffusion, and the amplification factor is positive (R > 0). Similarly, decay of the composition fluctuation when  $T > T_s$  requires that the interdiffusivity is positive ( $\check{D}_B > 0$ ) for downhill diffusion, and the amplification factor is negative (R < 0). Accordingly, from Equations (A4), (A6) and (A7), growth of the composition wave amplitude within the spinodal occurs when f'' < 0 and K > 0, whereas decay outside the spinodal occurs when f'' > 0 and K < 0. Since all diffusion coefficients are derived from the direct measurement of the amplification factor R as seen in Equation (A4), the computation of the gradient energy coefficients is approached by using the R variation with B. The value of R approaches zero for the infinite wavelength case, i.e., B = 0, that provides a unique boundary condition which is used in the interpolative analysis of data. The variation of R with B is simulated using a higher-order polynomial expansion.

$$R_{\rm s} = \Sigma k'_{\,\,\mu} \cdot B^{\,\mu}(h) \tag{A12}$$

From Equations (A4) and (A6), it follows that the difference  $\Delta R$  between the simulated value of the amplification factor  $R_s$  and the experimental value  $R_e$ , i.e.,  $\Delta R = R_s - R_e$ , will be positive for all temperatures and attributable as a sole consequence of strain energy. It has been shown [18] that the strain energy accelerates diffusion outside the spinodal, but hinders it within the spinodal. So, the simulated variation of R with B must envelope all experimental data as an upper bound. In addition, for decay it is already seen from Equation (A12) that  $\partial R/\partial B < 0$  as evaluated at B = 0, and for growth that  $\partial R/\partial B > 0$ . These  $\partial R/\partial B$  requirements guide the fitting procedure to determine the order  $\mu$  of the polynomial to appropriately provide the correct ( $\pm$ ) sign of the first  $k'_{\mu}$  term from Equation (A12), i.e.,  $k'_1 < 0$  for decay and  $k'_1 > 0$  for growth. The  $k'_{\mu}$  terms as determined from Equation (A12) are next used to compute the simulated values for interdiffusivity  $\check{D}_{Bs}$  that correspond with Equation (A4) as follows.

$$\check{D}_{Bs} = -R_s/B^2(h) \tag{A13}$$

The simulated  $\check{D}_{Bs}$  values are then curve fit using Equation (A8) to evaluate the  $K'_{\mu}$  values corresponding to the fit of the *R* variation with *B*. Since  $K'_{\mu}$  is equal to  $2K_{\mu}/f''$  from Equations (A7) and (A8), it follows that a general condition for growth is  $K'_1 > 0$  (since f'' < 0, D < 0 and  $K_1 > 0$  within the spinodal), whereas the condition for decay is  $K'_1 < 0$  (since f'' > 0, D > 0 and  $K_1 < 0$  outside the spinodal). From Equations (A6)–(A8), it follows that the difference  $\Delta D_B$  between the experimental value of the interdiffusion coefficient  $\check{D}_{Be}$  and the simulated value  $\check{D}_{Bs}$ , i.e.,  $\Delta \check{D}_B = \check{D}_{Be} - \check{D}_{Bs}$ , will be positive for all temperatures and is a sole consequence of strain energy. Again, strain energy [20] accelerates diffusion outside the spinodal and hinders it within the spinodal. So, the simulated variation of the magnitude of the interdiffusivity  $|\check{D}_B|$  with B must envelope all experimental data as a lower bound. The predetermined  $K'_{\mu}$  values that follow from evaluating Equation (A8), as consistent with the Equation (A12) data fit, are used to determine the one remaining, unknown diffusion parameter, i.e., D, at each temperature. The determination of the  $K'_{\mu}$  values by curve fitting both the amplification factor and interdiffusivity variation with wavenumber allows for the computation of the strain energy term. A plot of the strain energy term  $2\eta^2 \cdot \gamma$  is made to evaluate its variation with composition wavelength  $\lambda$ . The strain energy is determined by equating the difference between Equations (A6) and (A13) according to the following expression.

$$F_{\rm e}(h) = 2\eta(h)^2 \cdot Y(h) = \Delta \check{D}_B \cdot [f''(h)/\check{D}]$$
(A14)

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