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Citation: *Journal of Applied Physics* **107**, 014313 (2010); doi: 10.1063/1.3275052

View online: <http://dx.doi.org/10.1063/1.3275052>

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Structural and vibrational properties of Co nanoparticles formed by ion implantation

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(Received 1 October 2009; accepted 11 November 2009; published online 7 January 2010)

We report on the structural and vibrational properties of Co nanoparticles formed by ion implantation and thermal annealing in amorphous silica. The evolution of the nanoparticle size, phase, and structural parameters were determined as a function of the formation conditions using transmission electron microscopy, small-angle x-ray scattering, and x-ray absorption spectroscopy. The implantation fluence and annealing temperature governed the spherical nanoparticle size and phase. To determine the latter, x-ray absorption near-edge structure analysis was used to quantify the hexagonal close packed, face-centered cubic and oxide fractions. The structural properties were characterized by extended x-ray absorption fine structure spectroscopy (EXAFS) and finite-size effects were readily apparent. With a decrease in nanoparticle size, an increase in structural disorder and a decrease in both coordination number and bondlength were observed as consistent with the non-negligible surface-area-to-volume ratio characteristic of nanoparticles. The surface tension of Co nanoparticles calculated using a liquid drop model was more than twice that of bulk material. The size-dependent vibrational properties were probed with temperature-dependent EXAFS measurements. Using a correlated anharmonic Einstein model and thermodynamic perturbation theory, Einstein temperatures for both nanoparticles and bulk material were determined. Compared to bulk Co, the mean vibrational frequency of the smallest nanoparticles was reduced as attributed to a greater influence of loosely bonded, undercoordinated surface atoms relative to the effect of capillary pressure generated by surface curvature. © 2010 American Institute of Physics.

[doi:10.1063/1.3275052]

I. INTRODUCTION

Nanometer-sized particles or nanoparticles (NPs) have many potential technological applications due to their unique size-dependent properties. Deviations from bulklike behavior result from the large fraction of atoms at the NP surface and the finite number of atoms within each particle. Co NPs are of interest due to their enhanced magnetic¹ and optical properties,² both of which depend on NP shape, size, phase, and structure. Ion beam synthesis (IBS) has many advantages over other NP formation techniques and has been widely used for the fabrication of embedded NPs.³ The versatility of IBS stems from the ability to (i) introduce effectively any impurity into the desired matrix without solid solubility limitations and (ii) control the implanted ion concentration and depth within the matrix by manipulation of the implantation fluence and energy, respectively.

The size and crystallographic structure of Co NPs is governed by their route of formation,^{4–6} thermal history^{7,8} and host matrix.^{9,10} Using solution-based formation techniques, four different crystal structures of Co NPs have been formed: the hexagonal closed packed (hcp) and face-centered cubic (fcc) phases (stable in bulk material at room and high temperatures, respectively) plus the body-centered cubic and epsilon (ϵ) phases.^{11–14} Each phase exhibits characteristic

magnetic and optical properties,^{12,13} and the shape, size, and structure are correlated with the ligands or coatings.¹¹ For Co NPs formed by IBS in amorphous silica (SiO_2), the hcp and fcc phase fractions are influenced by the implantation and annealing conditions.^{5,7,15}

In this study, we seek to characterize the evolution of Co NPs as a function of the formation conditions to better define the relative influences of the processing parameters. Using the synchrotron-based techniques of small-angle x-ray scattering (SAXS), x-ray absorption near-edge structure (XANES), and extended x-ray absorption fine structure (EXAFS) in combination with transmission electron microscopy (TEM), we evaluate the variation of the size, phase, and structural parameters. We also use EXAFS to probe the vibrational properties of Co NPs and to determine the size- and phase-dependent Einstein temperatures. The experimental and analytical conditions are detailed in Sec. II. In Sec. III, we present the results and discussion followed by a conclusion in Sec. IV.

II. EXPERIMENT

Co ions were implanted at either liquid- N_2 temperature or 400 °C into 2- μm -thick SiO_2 layers thermally grown on Si (100) substrates. Implantation energies ranged from 416 to 1400 keV with fluences varying from 3.8×10^{15} to 3.0×10^{17} ions/ cm^2 , as listed in Table I. The resulting peak Co

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TABLE I. Summary of Co implantation parameters showing the implantation fluence ($\times 10^{16}$ ions/cm²) as a function of implantation energy E (keV). All implants were performed at liquid-N₂ temperature with the exception of those implanted at 416 keV and 400 °C.

$E=416$	$E=500$	$E=750$	$E=1000$	$E=1400$	Peak Co concentration (at. %)
...	0.38	0.38	0.57	1.04	0.3
...	1.14	1.14	1.71	3.14	0.9
...	...	4.40	4.80	10.60	3.0
...	...	...	30.00	...	9.0
7.0	...	...	...	...	4.0
8.0	...	...	...	...	4.5

concentrations ranged from 0.3 to 9.0 at. %. Samples were then annealed at 500–1100 °C in forming gas (5%H₂ + 95%N₂) for 1 h. Cross-sectional TEM measurements were performed with a Phillips CM300 microscope operating at 300 kV to study the NP shape and size.

For the synchrotron measurements, a unique sample preparation method¹⁶ was used to isolate the thin SiO₂ layer containing the Co NPs: the Si substrate was removed through mechanical grinding and selective wet chemical etching with KOH, and then multiple SiO₂ layers were stacked together between two Kapton windows. As a consequence, considerable NP material was concentrated within the sample holder, scattering from the Si substrate was eliminated, and high-resolution measurements were enabled.

Co standards were prepared by thermal evaporation of a Co film (2500 Å) onto a SiO₂/Si wafer followed by the plasma-enhanced chemical vapor deposition of a SiO₂ capping layer (3000 Å). To produce hcp material, samples were annealed at 400 °C in N₂ to remove disorder and any residual fcc component. fcc material was prepared by rapid thermal annealing at 900 °C in N₂ followed by rapid quenching. The purity of each phase was confirmed with x-ray diffraction.

Transmission SAXS measurements were performed at beamline 15ID-D of the Advanced Photon Source, Argonne, IL, using 11.27 keV x rays (1.1 Å wavelength). The scattering intensity $I(Q)$, where Q is the scattering vector, was collected for 5 s at a camera length of 1871 mm. A scattering spectrum from an unimplanted SiO₂ layer was subtracted from all NP spectra. The maximum entropy method¹⁷ (MEM) was used to determine the NP size distribution. Spherical particles were assumed consistent with TEM analysis.

Fluorescence-mode XANES and EXAFS measurements were performed at beamline 20-B of the Photon Factory, Japan. Samples were measured at the Co K -edge (7.709 keV) between temperatures of 15 and 300 K. Spectra were recorded using a 6×6 pixel-array Ge detector with the Si (111) monochromator detuned by 50% for harmonic rejection. Data were collected to a photoelectron wavenumber (k) value of 17 Å⁻¹. For energy calibration, a Co hcp reference foil was simultaneously measured in transmission mode.

Background subtraction, spectra alignment, and normalization of the EXAFS data were performed with ATHENA.¹⁸ The position of the Co edge was determined from the maximum of the first derivative of the absorption spectra. Isolated

EXAFS spectra were then Fourier-transformed (FT) over a k range of 3.3–15.3 Å⁻¹ with an adaptive Hanning window and back FT over a non-phase-corrected radial distance (R) range of 1.6–2.7 Å to isolate the first nearest neighbor (NN) shell. Structural parameters were determined with ARTEMIS (Ref. 18) utilizing the IFEFFIT (Ref. 19) code with theoretical scattering amplitudes and phase shifts calculated *ab initio* with the FEFF8 code.²⁰ The amplitude reduction factor (S_0^2) was determined for the hcp metal standard (0.80 ± 0.02) and then fixed for the subsequent fitting of all NP spectra. Following previous reports,^{10,21–23} the energy shift parameter (ΔE_0) was floated for the standards and NP samples. The coordination number (CN) was set to 12 for the fcc and hcp standards and floated for the NP samples. The bondlength (BL), Debye–Waller (DW) factor, and third cumulant (C_3) also floated during the fitting. All data sets were fitted with multiple k -weights of 1–4 to reduce interparameter correlation.

For the measurement-temperature-dependent EXAFS analysis, the evolution of the first NN structural parameters was determined by analyzing each data set over the 15–300 K temperature range individually with the CN and ΔE_0 fixed to the values determined at 15 K. The BL, C_3 , and DW factors were allowed to vary freely, and the temperature dependence of the DW factor was fitted with the Einstein model [Eq. (3)] to determine the static and temperature-dependent contributions to the total DW factor.

III. RESULTS AND DISCUSSION

As representative examples, Porod plots [$I(Q)Q^4$] and background-subtracted and fitted SAXS spectra for the 9.0 at. % samples are shown in Figs. 1(a) and 1(b), respectively, as a function of annealing temperature. In the former, the asymptotic behavior at high Q is characteristic of spherical metallic NPs embedded in a low-mass matrix and a slope of 4 (−4 in log-log plots) is consistent with scattering from a smooth, spherical surface.^{24,25} In the latter, the Q range for fitting is highlighted, as appropriate for the specific size distribution, with the experimental data clearly well fitted with the MEM. Normalized, volume-weighted size distributions are shown in Figs. 2(a) and 2(b) as functions of temperature and concentration, respectively. Clearly the NPs increase in size with temperature and concentration consistent with an Ostwald ripening process. Comparable size distributions were attained from TEM analysis which also demonstrated

FIG. 1. (a) Porod plots vertically offset for clarity and (b) background-subtracted SAXS intensities (fitted region shown in gray with spectra offset for comparison) for the 9.0 at. % samples as a function of annealing temperature.

that the NPs were of spherical shape with no evidence of faceting. Representative TEM images for the 9.0 at. % samples annealed at different temperatures are displayed in Fig. 3. From a Gaussian fit to the size distributions determined with SAXS and TEM, the centroid was used for the listed mean NP size. In the presence of considerable asymmetry, the statistical mean was instead used. All structural parameters are listed in Table II.

FIG. 2. Normalized and volume-weighted NP size distributions deduced from SAXS analysis as a function of (a) annealing temperature (for 9.0 at. % with inset at 1100 °C) and (b) Co concentration (for 800 °C).

FIG. 3. TEM images for the 9.0 at. % samples annealed at different temperatures: (a) as-implanted, (b) 500 °C, (c) 800 °C, and (d) 1100 °C.

Figure 4 shows the Arrhenius plot of the squared mean NP radius for all samples and two distinct temperature regions are observed. For the low temperature region, an activation energy of 0.03 ± 0.02 eV was calculated for both the 9.0 and 3.0 at. % samples. This athermal value was attributed to the irradiation-enhanced diffusion at temperatures where thermally induced diffusion is minimal or negligible. At temperatures higher than 500 °C, the activation energy of 0.59 ± 0.03 eV (average activation energy for all concentrations as the individual activation energy for each concentration were found to be the same within error) was slightly lower relative to that determined for Co NPs formed by annealing thin SiO_2/Co multilayer films (0.67 eV).²⁶ In this temperature region, the increase in average NP size was attributed to the increase in Co diffusion and aggregation.

The evolution of the phase fractions was measured with XANES as a function of annealing temperature. For the bulk standards and two concentration extremes (0.3 and 9.0 at. %), representative Co *K*-edge spectra are shown in Fig. 5, while the fcc, hcp, and oxide fractions are shown in Fig. 6, the latter calculated from a linear combination of the standards over photon energies ranging from 15 eV below to 50 eV above the edge. The absorption edges for the CoO and Co_3O_4 standards are shifted to higher energy due to the increase in Co atom valence. Pre-edge features are also apparent and result from a $1s$ to $3d$ transition of the photoelectron into a Co–O molecular-type orbital with intense *p*-type character.^{27,28} For the low-concentration, unannealed samples, the XANES spectrum is similar to that of Co_3O_4 , including the shift to higher energy, as consistent with Fukimi²⁹ and Cattaruzza *et al.*,³⁰ who reported that Co atoms in an as-implanted/as-deposited, NP-free state prefer a tetrahedral arrangement in SiO_2 similar to that in Co_3O_4 . In contrast, a metallic environment is evident in Fig. 5 for the high-concentration, unannealed sample, indicative of NP

TABLE II. Refined EXAFS fitting parameters and SAXS size distributions. ΔE , BL, DW, CN, and C_3 are the energy shift parameter, BL, DW factor, CN, and third cumulant, respectively.

Sample	Annealing temperature (°C)	ΔE (eV)	BL (Å)	DW (10^{-3} Å ²)	CN (atoms)	C_3 (10^{-5} Å ³)	Size (Å)
fcc bulk		0	2.491 (0.002)	2.98 (0.14)	12(fixed)	−3.9 (3.3)	
hcp bulk		0	2.481 (0.002)	2.73 (0.10)	12(fixed)	−2.2 (2.4)	
9.0 at. %	1100	−1.20(0.52)	2.488 (0.004)	2.64 (0.14)	11.2 (0.3)	−4.0 (3.7)	174 ^b
	800	−2.13(0.57)	2.469 (0.005)	3.74 (0.17)	9.7 (0.3)	−9.3 (2.3)	40 (9)
	500 ^a		n/m	n/m	n/m	n/m	22 (4)
	0 ^a		n/m	n/m	n/m	n/m	21 (5)
4.5 at. %	400	−0.40(0.6)	2.479 (0.004)	3.20 (0.14)	11.0 (0.3)	−5.2 (1.2)	52 (12)
4.0 at. %	400	−1.78(0.54)	2.473 (0.006)	3.61 (0.20)	10.6 (0.3)	−5.8 (1.9)	49 (10)
3.0 at. %	1100	−1.40(0.46)	2.490 (0.004)	2.75 (0.12)	11.7 (0.3)	−6.0 (1.3)	132 (37)
	800	−1.91(0.65)	2.464 (0.006)	4.43 (0.21)	9.2 (0.3)	−11.6 (2.8)	32 (7)
	500 ^a		n/m	n/m	n/m	n/m	19 (4)
	0 ^a		n/m	n/m	n/m	n/m	14 (3)
0.9 at. %	1100	−1.47(0.47)	2.483 (0.004)	2.96 (0.13)	11.7 (0.3)	−7.7 (1.7)	115 (28)
	800	−3.07(0.61)	2.456 (0.009)	5.59 (0.34)	8.1 (0.4)	−15.8 (4.6)	28 (5)
	500 ^a		n/m	n/m	n/m	n/m	17 (4)
0.3 at. %	1100	−1.14(0.47)	2.485 (0.004)	3.04 (0.12)	11.4 (0.2)	−3.4 (1.6)	114 (25)
	800	−3.28(0.65)	2.453 (0.01)	5.78 (0.36)	7.6 (0.4)	−18.3 (5.0)	21 (5)
	500 ^a		n/m	n/m	n/m	n/m	17 (5)

^aSamples that have significant oxide signal.^bThis sample has a non-Gaussian size distribution (Fig. 2) and this number represents the mean statistical value.

formation even in the as-implanted state. Figure 6 clearly shows the fraction of Co atoms in an oxidized environment decreases as a function of annealing temperature as expected. For all Co concentrations, the oxidized fraction is converted to the hcp phase with an increase in annealing temperature. The hcp phase fraction reaches a maximum at intermediate temperatures, above which the fcc phase fraction grows at the expense of the hcp material, consistent with the thermally driven hcp-to-fcc phase transformation. Note that bulk Co has two allotropic forms—hcp is stable at room temperature but transforms to fcc at temperatures >420 °C.^{31–33} For Co NPs formed by IBS in SiO₂, Fig. 6 shows that some or all of the transformed Co NPs retain the fcc phase upon post-annealing cooling to room temperature. Similar observations have been reported for bulk material where the reverse fcc-

to-hcp phase transformation is typically incomplete with residual fcc structure observable at room temperature.^{32,34,35} For Co NP samples with concentrations of 3.0–9.0 at. %, *all* NPs retain the fcc phase at room temperature after annealing at 1100 °C. Finite-size effects and/or the embedding matrix must perturb the fcc-to-hcp phase transformation in Co NPs. Zhao *et al.*⁸ attributed the stability of the fcc phase at room temperature to surface-curvature-induced capillary pressure inhibiting the transformation back to the hcp phase. From our EXAFS data described below, we are indeed able to calculate an enhanced surface tension relative to the bulk consistent with the mechanism of Zhao *et al.*⁸

The surface-energy calculations of Kitakami *et al.*⁴ for freestanding Co NPs suggest that the fcc and hcp phases are most stable for NPs of size <200 and >400 Å, respectively. The latter is intuitive as the properties of larger NPs must tend to bulklike. Our results show an opposite trend—smaller NPs are typically hcp while their larger counterparts are fcc. Clearly NP size is not the only factor influencing phase stability and we suggest that the influences of implant concentration, thermal history, and embedding matrix are non-negligible. In Fig. 7, we combine data from the present report with that from previous studies^{1,2,5,7} of Co NPs formed in SiO₂ by IBS at similar implantation temperatures (at 21 °C or less) and annealing conditions to demonstrate the predominant phase is a function of the implantation and annealing conditions. Clearly the fcc phase is only retained upon cooling to room temperature in NPs formed by high concentration (>1.8 at. %) and high temperature annealing to produce large NPs.

Figures 8(a), 8(c), and 8(e) show representative k^3 -weighted EXAFS spectra as a function of annealing temperature and concentration. The amplitude increases with an

FIG. 4. Arrhenius plot of the squared mean NP radius (R^2) as a function of the inverse temperature (k_B is the Boltzmann constant and T is the annealing temperature). The solid lines are linear fits to the experimental data.

FIG. 5. XANES spectra at the K -edge for (a) bulk standards, (b) all 9.0 at. % samples, and (c) all 0.3 at. % samples.

increase in either parameter, consistent with the previously demonstrated increase in NP size. From a comparison with the two standards, the largest NPs are clearly bulklike. Figures 8(b), 8(d), and 8(f) show the corresponding phase-corrected FT spectra with refined structural parameters listed in Table II. As above, the amplitude increases with an increase in either temperature or concentration due to, as we

FIG. 6. Fitted hcp, fcc, and oxide fractions as a function of annealing temperature for (a) all 9.0 at. % samples and (b) all 0.3 at. % samples.

discuss below, an increase in average CN and decrease in structural disorder. In Fig. 9, we correlate the four refined structural parameters (from EXAFS) with the mean NP size

FIG. 7. Summary of the crystallographic phase (measured at room temperature) of Co NPs formed by IBS determined from the current study (open symbols) and Refs. 1, 2, 5, and 7 (solid symbols) as functions of annealing temperature and (a) NP size and (b) of implant Co concentration.

FIG. 8. [(a), (c), and (e)] k^3 -weighted EXAFS spectra (offset for comparison) and corresponding phase corrected FT EXAFS spectra [(b), (d), and (f)] for bulk standards; all 1100 °C and all 800 °C samples.

(from SAXS). The four structural parameters are clearly size dependent, demonstrating that finite-size effects are operative and measurable for our given range of NP diameters. As anticipated, all structural parameters tend toward those of the bulk standards with an increase in NP size.

The average CN can be calculated for a spherical 12-fold coordinated NP as a function of NP size from³⁶

$$CN = 12[1 - (3/2D)R_B], \quad (1)$$

where D is the NP diameter and R_B is the bulk fcc BL. As the NP size decreases, the relative fraction of undercoordinated surface atoms increases and thus the average CN decreases. In Fig. 9(a), the experimental data are well fitted with the theoretical estimate.

The DW factor includes both structural and thermal contributions. For our two standards (see Table II), we attribute the greater value measured for fcc material to the preparation method, which included both a rapid annealing and quench. For the NPs, a decrease in size yields an increase in the relative fraction of surface atoms as before, and an increase in structural disorder as apparent from Fig. 9(b). For semiconductor NPs embedded in SiO₂, simulation³⁷ and experiment³⁸ have demonstrated that the interfacial atom environment is highly distorted and such atoms relax or reconstruct to accommodate material and bonding differences across the interface. A similar trend has been reported for other embedded elemental metal NPs.^{39–41}

The structural parameter C_3 is a measure of the asym-

FIG. 9. Structural parameters of the first NN shell showing (a) CN, (b) DW factor, (c) third cumulant (C_3), and (d) BL as a function of NP size. The solid line in (a) is the CN derived from Eq. (1). The insets in (b) and (c) show the same data plotted as inverse diameter. The inset in (d) shows the BL contraction relative to the bulk fcc Co standard as a function of inverse NP diameter with the solid line as a fit to Eq. (2)

metric deviation from a Gaussian interatomic distance distribution and a negative value indicates that the BL distribution is skewed toward shorter BLs. The latter results from contracted bonds associated with surface/interfacial atoms, the relative fraction of which increase with a decrease in NP size. Accordingly, the magnitude of C_3 thus increases with a decrease in NP size as apparent from Fig. 9(c). Plotting the data of Figs. 9(b) and 9(c), the DW factor and C_3 , respectively, as a function of inverse NP diameter (insets of Fig. 9) shows that these two parameters scale as a function of the surface-area-to-volume ratio.

Figure 9(d) readily demonstrates a mean BL contraction as the NP size decreases. This contraction is the result of capillary pressure induced by surface curvature, where the former is proportional to inverse NP size. Simulations for elemental metal NPs (Ref. 42) show that pressures in excess of 1.5 GPa can be achieved. The inset of Fig. 9(d) plots the same data as a function of inverse NP diameter ($1/D$). Using a simple liquid drop model,⁴³ the surface tension (f) is calculable from

$$\Delta R = -4/3KR_b f(1/D), \quad (2)$$

where ΔR is the relative BL contraction, K is the bulk compressibility, and R_b is the bulk BL. Using K and R_b for bulk hcp Co yields a surface tension of 5.1 ± 0.1 J/m² for Co NPs, a value significantly larger than that reported for bulk hcp and fcc Co (2.79 and 2.73 J/m², respectively)⁶ [Fig. 9(d) includes data for both fcc and hcp NPs]. Phase-specific fits yielded similar values within experimental error. Other elemental metal NPs embedded in SiO₂ exhibit a similar

trend [Cu,⁴⁰ Pt³⁹ and Au (Ref. 41)]. In bulk Co, surface tension does not inhibit the fcc-to-hcp transformation. However, the Co NPs characterized herein are significantly perturbed relative to bulk material—their compressive state and enhanced surface tension yields not only a BL contraction but, as suggested by Zhao *et al.*,⁸ a means of inhibiting the fcc-to-hcp transformation and thus stabilizing fcc Co NPs at ambient conditions.

Temperature-dependent k^3 -weighted EXAFS spectra with corresponding phase-corrected FTs are presented in Fig. 10 for bulk hcp Co and both 52 and 28 Å diameter hcp Co NPs. In general, the amplitude decreases with an increase in measurement temperature due to the increase in thermal disorder while, as above, at a given temperature, the amplitude for bulk material exceeds that for NPs due to the reduced CN and enhanced structural disorder associated with NPs.

An Einstein model^{20,44,45} is commonly used in the analysis of temperature-dependent EXAFS data to describe the thermal evolution of the DW factor. As described above, the DW factor includes both structural (σ_S^2) and thermal (σ_T^2) contributions with the former assumed temperature independent. Figure 11(a) shows the DW factor as a function of measurement temperature and includes a fit with a correlated anharmonic Einstein model⁴⁶ given by

$$DW = \sigma_S^2 + \sigma_T^2,$$

FIG. 10. [(a), (c), and (e)] k^3 -weighted EXAFS spectra and [(b), (d), and (f)] FT spectra for bulk hcp Co, and 52 and 28 Å diameter HCP Co NPs, all as a function of measurement temperature.

$$\sigma_T^2 = \frac{\hbar^2}{2\mu k_B \Theta_E} \frac{1 + \exp(-\Theta_E/T)}{1 - \exp(-\Theta_E/T)}, \quad (3)$$

where Θ_E is the Einstein temperature, T is the measurement temperature, k_B is Boltzmann's constant, $\hbar$ is Planck's constant divided by 2π , and μ is the reduced mass of the atomic pair under investigation. As described above, the increase in DW factor with measurement temperature is the result of an increase in thermal disorder. Table III lists values for Θ_E , σ_S^2 , and the effective bond-stretching force constant k_{eff} , the latter calculated using⁴⁵

$$k_{\text{eff}} = \mu k_B^2 \Theta_E^2 / \hbar^2. \quad (4)$$

Experimental data comparing the vibrational properties of bulk hcp and fcc Co is scant. Our measurements suggest they

FIG. 11. Thermal evolution of the FNN DW factors for the Co standards and NP samples. The solid lines are fits with a correlated anharmonic Einstein model [Eq. (3)].

TABLE III. Einstein temperature (Θ_E), structural disorder (σ_S^2), and effective bond-stretching force constant (k_{eff}).

Sample	Θ_E (K)	σ_S^2 ($10^{-3} \text{ \AA}^2$)	k_{eff} (N/m)
hcp foil	295 (1)	0.03(0.01)	72 (1)
fcc foil	286 (2)	0.28(0.05)	68 (1)
132 Å fcc NPs	285 (3)	0.04(0.01)	68 (1)
52 Å hcp NPs	291 (3)	0.46(0.06)	72 (1)
28 Å hcp NPs	280 (3)	2.76(0.10)	66 (2)

are subtly different, with Θ_E values of 295 ± 1 and 286 ± 2 K, respectively. If one considers the Einstein temperature as a measure of effective bond strength,⁴⁵ the data presented herein is indicative of slightly stronger metallic bonds in the hcp phase compared to the fcc phase. The validity of such a difference is supported by our findings for 52 Å diameter hcp and 132 Å diameter fcc NPs, which yield Θ_E values of 291 ± 3 and 285 ± 3 K, respectively. Recall from Fig. 9 that the structural properties of these NPs were near bulklike. Clearly their vibrational properties are also near bulklike including the subtle phase-specific difference in Θ_E . Finite-size effects are more apparent in the vibrational (and structural) properties of smaller NPs. 28 Å diameter hcp NPs exhibit a Θ_E value of 280 ± 3 K. Relative to bulk hcp material, the reduction in Θ_E reflects a lower mean vibrational frequency and softening of the metallic bonds in the NP sample. Simulations for elemental metallic NPs show capillary pressure and disordered surface atoms shift the vibrational density of states (VDOS) in opposite directions—to higher and lower frequencies, respectively.⁴² Our results thus indicate that surface/interfacial disorder is the dominant influence on the vibrational properties of Co NPs. A similar size-dependent trend in the Debye temperature values was reported for fcc Co NPs embedded in a crystalline Ag matrix.⁴⁷

IV. CONCLUSIONS

In summary, the influence of the processing conditions on the structural and vibrational properties of Co NPs has been investigated with SAXS, TEM, XANES, and EXAFS measurements. As anticipated, the NP size increased as a function of both implantation fluence and annealing temperature. Co atoms in an initially oxidized state were progressively converted to the metallic hcp and fcc phases with an increase in temperature. The relative fraction of hcp and fcc phases was governed by both concentration and annealing temperature. Finite-size effects were readily apparent in the Co NP structural properties including a reduction in average CN and BL plus enhanced structural disorder and asymmetrical deviation from a Gaussian-like interatomic distance distribution. The size-dependent contraction in the BL was the result of a surface tension of more than twice the bulk value. This enhanced surface tension may well inhibit the fcc-to-hcp transformation in Co NPs as they cool to room temperature.

Using a correlated anharmonic Einstein⁴⁶ model, subtle differences were first apparent in the bulk hcp and fcc stan-

dards. Finite-size effects were also evident in the Co NP vibrational properties. A reduction in Einstein temperature or equivalently weaker bonding relative to bulk material was measurable in the smallest NPs. The relative influence of loosely bonded and undercoordinated surface/interfacial atoms on the VDOS must thus be greater than that due to capillary pressure.

ACKNOWLEDGMENTS

This work was financially supported by the Australian Synchrotron and the Australian Research Council. ChemMatCARS Sector 15 is principally supported by the National Science Foundation/Department of Energy under Grant No. NSF/CHE-0822838. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

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