

## Low-Frequency Vibrational Properties of Nanocrystalline Materials

P. M. Derlet,<sup>1</sup> R. Meyer,<sup>2</sup> L. J. Lewis,<sup>2</sup> U. Stuhr,<sup>1</sup> and H. Van Swygenhoven<sup>1</sup>

<sup>1</sup>*Paul Scherrer Institute, 5232 Villigen, Switzerland*

<sup>2</sup>*Département de Physique et Groupe de Recherche en Physique et Technologie des Couches Minces (GCM), Université de Montréal, CP 6128 Succursale Centre-Ville, Montréal (Québec) H3C 3J7, Canada*

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The vibrational density of states (VDOS) of bulk nanocrystalline Ni and Cu (model) samples with grain diameters between 5 and 12 nm are derived from molecular-dynamics simulations. The results show an enhancement of the density of states at low and high energies. Because of large system sizes and a decomposition of the VDOS into grain and grain-boundary components, the low-frequency region can be investigated for the first time. It is found that the anomalous increase of the VDOS is mainly caused by the high number of grain-boundary atoms and that a power-law behavior of the low-frequency grain-boundary VDOS exists, which suggests a reduced dimensionality effect.

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The vibrational density of states (VDOS) of nanocrystalline (nc) materials exhibits a low-frequency enhancement when compared with their coarser-grained counterparts. This feature has been established experimentally using thermal neutron scattering from which the time-of-flight spectra can directly give the VDOS  $g(\omega)$  [1–6]. More recently, the strong incoherent neutron scattering component from hydrogen was used to directly probe the VDOS contribution from the grain-boundary region [7]. It was found that in the low-frequency limit the grain-boundary component of the VDOS exhibits  $g(\omega) \sim \omega$ , rather than the usual quadratic dependence. This suggests that the increase in low-frequency modes arises from atoms at grain boundaries and/or surfaces. Yet, the exact nature of the low-frequency enhancement of the VDOS remains unclear and we address this problem here using molecular-dynamics (MD) simulations.

Early MD work [8] on computer-generated nc samples already showed an increase of the VDOS at low frequencies; however, the small system size of 416 atoms did not allow the low-frequency VDOS to be probed and/or compared to experimental data. Moreover, the partial contributions of grains and grain boundaries were not resolved. In recent simulations of metallic nanoclusters [9,10], a separation was made between the VDOS from inside the cluster and that from the outer (surface) layers. The latter region does indeed show an enhancement at low frequencies; however, again, due to the inherently limited number of atoms, a detailed picture of the low-frequency VDOS could not be obtained.

In this Letter, we report on calculations of the VDOS for “model” nc materials in which we have separated the grain-boundary component of the VDOS from the contribution of the grains. Using two Ni and one Cu system, each with more than one million atoms and realistic grain sizes, we overcome the limitations of earlier work and get detailed information about the VDOS at low frequencies. The Ni samples have been used extensively in previous studies of grain-boundary structure [11,12] and the defor-

mation properties of nc materials [13–16]. They contain a fully three-dimensional grain-boundary network based on the Voronoi construction [17], which is believed to contain the essential geometry of nc materials. These configurations contain approximately  $1.2 \times 10^6$  atoms each and have average grain sizes of 5.2 and 12 nm, corresponding to 125 and 15 grains, respectively. The details of their preparation can be found elsewhere [11]. An important conclusion from the previous work is that, apart from scale, the grain-boundary structure is not fundamentally different from that of ordinary polycrystals [11,12]. In contrast to the Ni samples, the Cu configuration was obtained by the simulation of pressure-assisted sintering of Cu nanoparticles [18]. Starting from a random configuration of 100 particles with diameters between 4 and 10 nm, the formation of a nc system was simulated. After a maximum pressure of 2. GPa had been slowly released, an 87% sample density (of the perfect fcc crystalline value) was obtained. Most of the excess volume in this configuration is due to an open network of pores, leading to a considerable amount of internal surface area. This sample contains 100 grains giving a volume averaged grain size of 6.1 nm.

For samples containing more than a million atoms, the calculation of the VDOS via direct diagonalization of the harmonic force matrix becomes intractable. Therefore, we have determined the VDOS numerically via the Fourier transform of the velocity autocorrelation function (VACF) using the techniques described in [19]. Prior to the calculation of the VACF, the samples were equilibrated at 300 K using constant temperature MD within the Parrinello-Rahman scheme [20]. We employed the tight-binding potentials of Cleri and Rosato [21] which, although not fitted directly to bulk phonon properties, reproduce well the known phonon spectra of crystalline fcc Ni and Cu. The VACF was determined from simulation runs over periods ranging from 8 to 20 ps. For such a time period, some anharmonic atomic activity (atomic shuffling/diffusion) can be expected in the grain-boundary region. However,

such activity involving between 10 and 100 atoms is small at these time scales and its effect on the calculated VDOS can thus be neglected. In order to improve statistics, the final VDOS was averaged over several simulation runs.

In the present work, we identify the grain-boundary structure using a topological short range analysis [22], which assigns a local crystalline order to each atom. We separate the atoms, and thus the VDOS, into three groups: those atoms with fcc symmetry at least up to fourth nearest neighbor (perfect fcc: PFCC), those atoms with fcc symmetry at most up to the third nearest neighbor (good fcc: GFCC), and those atoms with other symmetry (grain boundary: GB). Figure 1 displays a selected area of the 12 nm Ni sample, in which the central region contains a triple junction. Using the three categories of bulk atoms, the grain-boundary region can easily be identified. In the case of our Cu results, we additionally classified atoms with coordination numbers  $Z < 10$  as surface atoms (SURF).

Figure 2 shows the total VDOS for the nc-Ni samples. The total VDOS's compare well to a recent experimental investigation of nc-Ni [6]. In addition, we also include the VDOS for a perfect (crystalline) fcc sample of comparable size. We see that, even at 300 K, the VACF technique reproduces well the Van Hove singularities in the transverse and longitudinal peak regions when compared with experiment [23]. For the nc VDOS, the enhancement at low phonon energies with decreasing grain size is clearly evident. In addition, there is also a broadening of the transverse and longitudinal peaks, together with an enhancement at higher phonon energies. The high-frequency tail for the calculated crystalline fcc VDOS is an anharmonic contribution due to the finite temperature of the MD simulations.

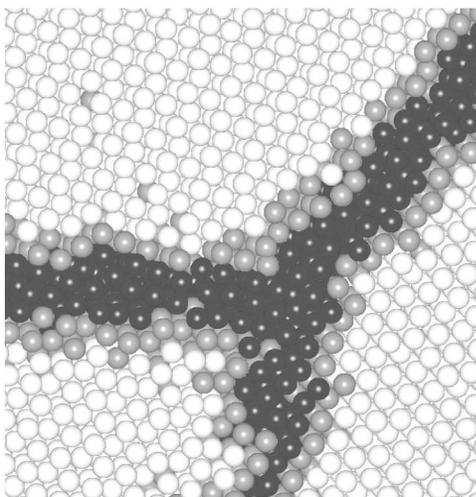


FIG. 1. Selected area of the 12 nm nc-Ni sample in which atoms have been shaded according to whether they are perfect fcc (fcc to at least fourth nearest neighbor)—white; good fcc (fcc to less than fourth nearest neighbor)—gray; or grain boundary atoms—black.

Figure 3 now resolves the total VDOS of the Ni samples into the normalized partial VDOS for the three contributions; PFCC, GFCC, and GB. It is remarkable that there is little difference between the components as a function of grain size. This is particularly the case for the GB VDOS, indicating that the grain-boundary structure does not fundamentally change with decreasing grain size. The GB VDOS exhibits little sign of the transverse and longitudinal peaks present in the fcc components and has a form akin to a significantly disordered state. This is to be expected due to the varying local environments within the grain-boundary regions. We see that it is the grain-boundary component which is primarily responsible for the low- and high-frequency enhancements of the total VDOS. Inspection of the PFCC VDOS reveals only slight broadening when compared to the crystalline fcc. Such observations have also been made in the case of nanoclusters [9,10]. For the GFCC VDOS, Fig. 3 reveals a more broadened spectrum than the PFCC atoms, with a small low-frequency enhancement. This is to be expected since the GFCC atoms can extend into the grain up to one lattice constant and thus couple strongly to the PFCC oscillation modes (see Fig. 1). Therefore, the GFCC atoms are of intermediate character between PFCC and GB, as evidenced by Fig. 3.

With the GB VDOS largely independent of grain size, the degree of anomalous features observed in the total VDOS will scale with the percentage of grain-boundary atoms. In the 5 nm Ni sample, 36% are grain-boundary atoms while there are 16% in the 12 nm sample. Thus, it is in the nanoscale, where the proportion of atoms belonging to the grain boundary is no longer negligible (unlike polycrystals), that the anomalous features of the GB VDOS can be resolved. We note that, for the Ni samples, there is a decrease in the number and type of grain boundaries with increasing grain size. That this does not influence our results was checked explicitly with the help of an independent 5.2 nm sample with the same number and orientation of grains as the 12 nm sample.

In Fig. 4 we present the partial VDOS for the nc-Cu sample. It can be seen that the PFCC, GFCC, and GB components show a similar behavior as in the nc-Ni samples.

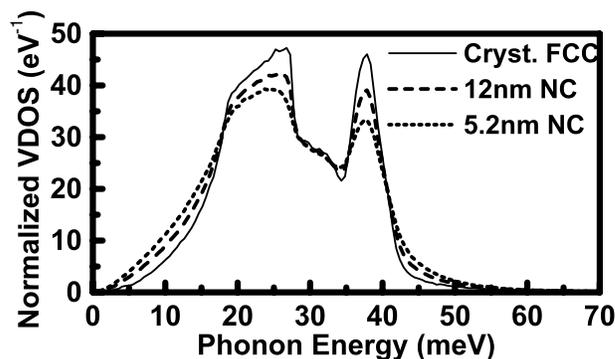


FIG. 2. Normalized total VDOS for nc Ni of average grain sizes 5 and 12 nm. Also shown is that for crystalline fcc Ni.

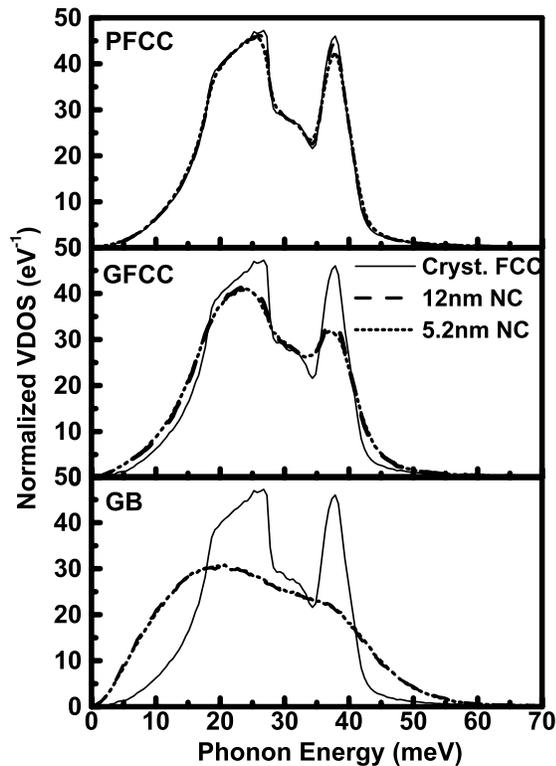


FIG. 3. Normalized partial VDOS for nc Ni of average grain size 5 and 12 nm: PFCC—perfect fcc; GFCC—good fcc; and GB—grain boundary atoms compared to crystalline fcc Ni. See text and Fig. 1 for more detailed definitions.

For the additional surface component in this system, we observe a rather intense increase of the VDOS at low energies and a significant decrease at medium and high energies. This is in contrast to the results obtained for the surface component of nanoparticles [9,10]. One possible

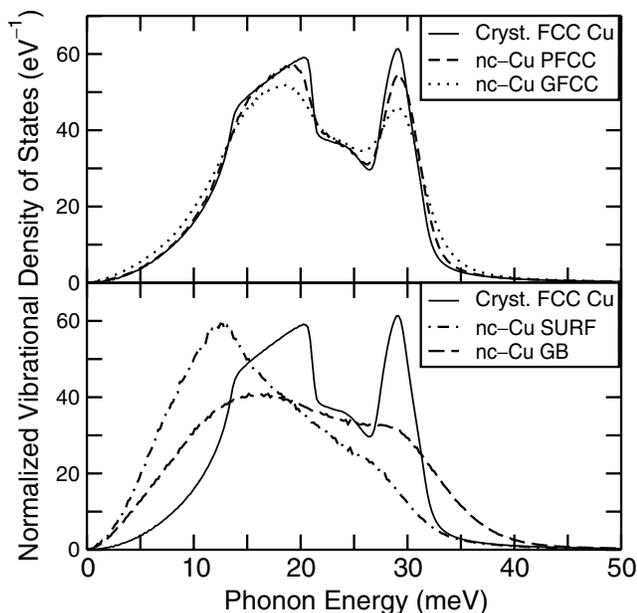


FIG. 4. Normalized partial VDOS of 87% dense porous nc Cu with an average grain size of 6.1 nm.

explanation for this discrepancy is the fact that here we identified only atoms with a strongly reduced coordination  $Z < 10$  as surface atoms. We chose this criterion since it includes atoms from typical surfaces such as (111) and (100) while excluding the high number of grain-boundary atoms with slightly reduced coordination. In contrast to this, the  $Z < 12$  criterion used in [9,10] includes subsurface atoms which couple more strongly to the innergrain oscillation modes. Note that the reduced coordination of the surface layer is known to affect the VDOS in a way similar to our results [24].

It has been speculated whether internal surfaces rather than the grain boundaries might cause the low-frequency enhancement of the VDOS in nc materials. We address this question in Fig. 5 in a most general way by simply comparing the dense 5.2 nm Ni sample with the porous 6.1 nm Cu system. Note that we used different scales for Cu and Ni in order to make the VDOS's directly comparable. It can be seen that apart from this scaling factor the two nc samples give nearly identical results. This coincidence cannot be explained by a compensation of the effect of surface atoms by the increased grain size at low phonon energies since this would lead to differences in the high-energy tail of the VDOS. The similarity of the VDOS therefore reflects the fact that the GB VDOS for both Ni and Cu is essentially identical (compare Figs. 3 and 4), and that, in spite of its low density, only a small fraction of the atoms in the Cu sample are actually located at the internal surfaces.

It remains to clarify the nature of lattice vibrations in nc materials in the low-frequency regime. Figure 6 reveals that in this regime the grain-boundary VDOS's of our nc samples are well accounted for by a power law with an exponent  $n$  of approximately 1.5, while the crystalline counterparts show the usual quadratic behavior. Such a noninteger power law has been used, with  $n = 1.22$ , to explain the temperature dependence of Mößbauer experiments on nc Fe [25]. Although at the present stage other explanations cannot be excluded, the exponents of 1.5 suggest a reduced effective dimensionality in the grain

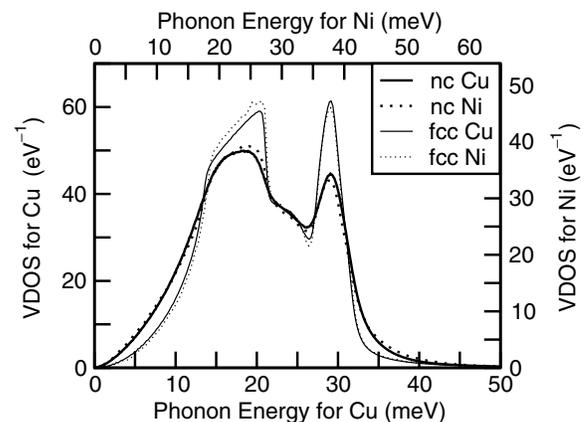


FIG. 5. Normalized total VDOS for the 6.1 nm nc Cu, the 5.2 nm nc Ni, and the corresponding perfect crystalline fcc systems.

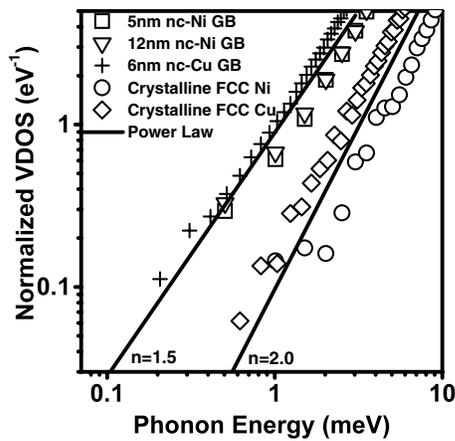


FIG. 6. Low energy part of the normalized grain boundary VDOS for the nc-Ni and nc-Cu samples together with the corresponding crystalline fcc systems. Also shown are power laws with exponents  $n = 1.5$  and  $2$ .

boundaries since the VDOS is expected to scale at low frequencies as  $\omega^{d-1}$ , where  $d$  is the spatial dimension [26]. This viewpoint is further supported by the observation that the integrated pair distribution function of the grain-boundary atoms in the Ni samples varies as  $r^{2.5}$  at distances  $r < 4$  nm. This is close to the result of Chadwick [27] who reports a spatial dimension  $d = 2.4$  for the grain boundaries in nc Pd.

In conclusion, we have investigated the vibrational spectrum of nc-Ni and nc-Cu model samples with grain sizes between 5 and 12 nm. The results show an enhancement of the VDOS at high and low phonon energies which increases with decreasing grain size. The separation of the VDOS in contributions from the grains, grain boundaries, and internal surfaces shows that these enhancements are mainly caused by the grain boundaries whereas the VDOS inside the grains is nearly unchanged. Internal surfaces play only a minor role with the possible exception of very low density materials with large grains. At low phonon energies, we find a power-law behavior of the grain boundary VDOS in the nc materials with an exponent smaller than two, suggesting a reduced dimensionality of the corresponding phonons.

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