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Polymorphic bcc to fcc transformation of nanocrystalline niobium studied by positron annihilation

P. P. Chattopadhyay*
Department of Metallurgical Engineering, Bengal Engineering College (D.U.), Howrah 711103, India

P. M. G. Nambissan†
Atomic & Nuclear Physics Division, Saha Institute of Nuclear Physics, Calcutta 700064, India

S. K. Pabi‡ and I. Manna§
Department of Metallurgical and Materials Engineering, Indian Institute of Technology, Kharagpur, West Bengal 721302, India

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Positron lifetime and Doppler broadening measurements on nanocrystalline niobium over a wide range of grain sizes (5–35 nm) were performed. Significant changes in the structure and properties of grain boundaries and intercrystalline regions were observed when the grain size was reduced below 10 nm. While positron lifetime at the grain boundaries sharply increased owing to an increase in the excess free volume associated with the atoms, the atomic reordering brought in a remarkable redistribution of the electron momenta at the grain boundaries. A model-based calculation of the excess free volume of atoms at the grain boundaries supported these findings. The calculated bulk modulus and the negative hydrostatic pressure predicted a lower size limit of ~2 nm for the mechanical and thermodynamic stability of the grain boundaries. Quantum confinement of the electron energy levels can be expected only below 20 K for grains of size above this limit.

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I. INTRODUCTION

In the recent works reported by some of us,[1,2] nanocrystalline niobium has been shown to undergo an irreversible bcc→fcc polymorphic phase transformation when the grain size was reduced below 10 nm during high-energy ball milling. The exact genesis of this transformation has been elusive despite having evidence in support of this observation from samples prepared in different media.[1] Since the majority of the atoms in nanocrystalline materials are located on the grain boundaries, a comprehensive study of the structure and properties of the grain boundaries can perhaps provide some insight into the mechanism responsible for this transformation. Positron lifetime and Doppler broadening measurements are expected to be promising in this context as positrons are highly susceptible for getting trapped in vacancies likely to exist in diffused form at the grain boundaries.[3–5]

The positrons on entering a solid will rapidly lose their kinetic energy via dissipative processes like electronic excitation and ionization, electron-hole pair creation, and phonon interaction.[6,7] The annihilation cross section becomes significant only at thermal velocities. As the positrons are able to survive for a few hundred picoseconds in the solid, their diffusion through the solid (due to the scattering from longitudinal acoustic phonons[8]) will be decisive in their trapping at the specific sites of eventual annihilation. The average diffusion length of thermalized positrons in metals is about 50–100 nm.[9,10] If the grain size is less than these dimensions, the positrons will diffuse out to the grain boundaries before annihilation. In nanocrystalline materials, therefore, the annihilation gamma rays will carry information about the structure of the grain boundaries and intercrystalline regions as all the positrons necessarily get annihilated at these sites only.

The measurement of the lifetimes of positrons will yield quantitative information about the diffused grain-boundary defects. It must be added that the thermalization will also make the linear momentum of the positron negligible compared to that of the electron. Hence the two annihilation gamma rays will suffer a Doppler shift $\Delta E = p_x c/2$ in their energy, where p_x stands for the electron momentum projected in the direction of detection of the gamma rays.[6] The integrated effect of detection of gamma rays with all possible ΔE values (over a finite duration of time) is an overall Doppler broadening of the annihilation gamma-ray spectrum. The effect is generally parametrized by dividing the counts integrated under a central segment spreading over ±600 eV by the counts under the full spectrum.[6] This parameter, usually denoted as S in defect structure analysis, is sensitive to the presence and growth of vacancy-type defects and interfaces in solids.[6]

II. EXPERIMENTAL DETAILS

Elemental niobium (Nb) powder having an average particle size of 50 μm was milled in a Fritsch P5 planetary ball mill at 300 rpm using hardened steel vials and balls with a ball-to-powder weight ratio of 10:1. A number of samples were prepared by milling for different intervals of time and were examined by x-ray diffraction using a Philips PW1710 diffractometer. A few illustrative patterns are shown in Fig. 1. The average grain size was determined from the peak broadening analysis using Scherrer equation[11] and the grain sizes for samples milled for different hours are shown in Fig. 2. Positron annihilation studies were conducted using a ^{22}Na source (~1.5 μCi) kept at the center of the column of the powdered sample taken in a glass tube. The glass tube was continuously evacuated during the experiments in order to eliminate the air otherwise trapped inside the powder. The sample covered the source from all sides over a thickness sufficient to ensure that all the positrons annihilated within the sample only. Positron lifetime measurements were car-

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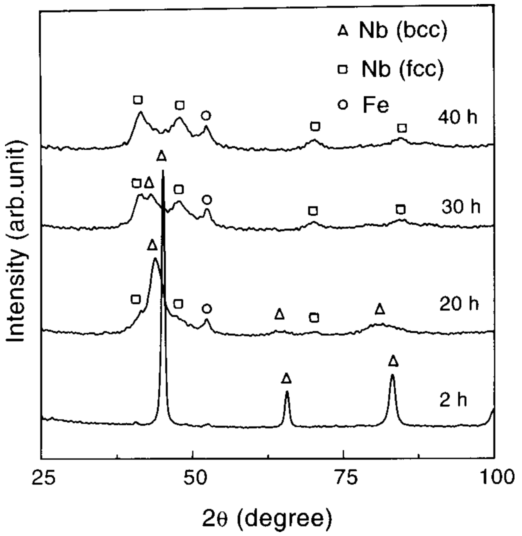

FIG. 1. X-ray diffraction patterns of nanocrystalline Nb obtained at different stages of high-energy ball milling.

ried out using a gamma-gamma ray coincidence spectrometer with a prompt time resolution [fullwidth at half maximum (fwhm)] ~ 240 ps. The positron lifetime spectra were analyzed using the computer programs RESOLUTION and POSITRONFIT.[12] An HPGe detector with a resolution of 1.14 keV at 514 keV (^{85}Sr) was used for Doppler broadening measurements.

III. RESULTS

The x-ray diffraction patterns of the samples milled for different intervals of time are shown in Fig. 1. It appears, as indicated by the shifting of peaks to the lower diffraction angles (2θ), that the grain lattice expands with increasing hours of milling and, as suggested by the positions of the peaks, the grains undergo a bcc to fcc phase transformation at lower grain sizes. In our previous works,[1,2] we had discussed a few other observations to clarify that the said transformation neither results from a possible contamination by Fe atoms (from the hardened steel vials and balls) nor from the presence of impurities like carbon or nitrogen (likely to dissolve from the atmosphere during the milling process). To further closely examine the evolution in the structure of elemental Nb during the different stages of ball milling, the lattice parameter a (obtained from Fig. 1) was plotted against the Nelson-Riley parameter[11]

$$N=\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta} \tag{1}$$

and the precise lattice parameter a_0 of the fcc phase was determined by extrapolating the line to $N=0$. The value of a_0 thus obtained was 0.428 nm. It is relevant to mention here that this is larger than $a_0=0.343$ nm of bcc Nb, implying that a significant lattice expansion accompanies the bcc→fcc transformation.

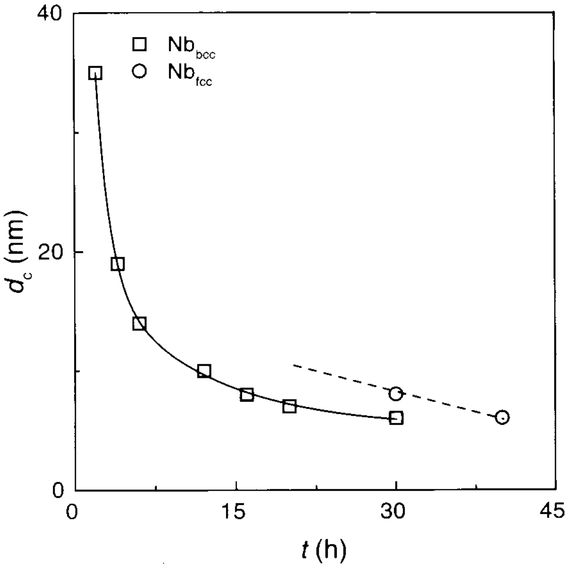

FIG. 2. The variation of the grain size d_c of Nb as a function of milling time t (in hours).

The positron lifetime spectrum of a coarse-grained Nb sample was initially recorded and analyzed. Expectedly the spectrum yielded a single positron lifetime ($\tau_b=138$ ps) resulting from the electron-positron annihilation in the bulk Nb structure. The spectra of the nanocrystalline samples were best fitted ($\chi^2\nu=1.05-1.20$, ν is the degrees of freedom[12]) with three positron lifetimes τ_1, τ_2, and τ_3 (with relative intensities I_1, I_2, and I_3) given by

$$N(t)=I_1e^{-t/\tau_1}+I_2e^{-t/\tau_2}+I_3e^{-t/\tau_3}. \tag{2}$$

The analysis encountered large statistical errors due to the relatively fewer number of counts defining the longer lifetime τ_3 (varying between 2.2 and 3.4 ns approximately) in all the samples. Hence a constrained fit was used where τ_3 was fixed at 2.8 ns, the average of the values obtained in the initial unconstrained analysis. We observed that the intensity I_3 is rather small ($\sim$0.8–1.0 %) and hence this lifetime component is not included in further discussion. The vast majority of the positrons entering the sample annihilated either with a lifetime τ_1 or with τ_2. Figure 3 illustrates the values of these lifetimes and intensity I_2 obtained in samples with different average grain sizes. The variation of the mean positron lifetime, defined as $\tau_m=(\tau_1I_1+\tau_2I_2)/(I_1+I_2)$, with grain size is shown in Fig. 4. We note that τ_m varies between 207 and 217 ps which is significantly larger than the bulk positron lifetime $\tau_b=138$ ps, implying that positrons in the nanocrystalline samples are trapped at sites with lower than average electron density compared to the bulk.

The variation of the Doppler broadened lineshape parameter S versus grain size is shown in Fig. 5.

IV. DISCUSSION

We note from Fig. 5 that the S parameter after 2 h of milling (mean grain size $\sim$35 nm) is about 5% larger than the reference value ($S=0.3464$ for coarse-grained Nb). This indicates a significantly enhanced annihilation of positrons from open-volume environments. Yet another evidence for this conclusion comes from the values of τ_1, which lie between that for coarse Nb ($\tau_b=138$ ps) and that for the small-

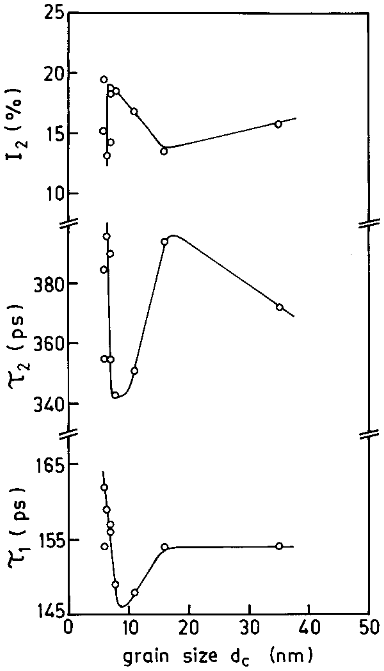

FIG. 3. The variation of positron lifetimes τ_1 and τ_2 and intensity I_2 with grain size in nanocrystalline Nb.

est open-volume defect in a crystalline solid, i.e., a monovacancy ($\tau_{1v} = 200\,\mathrm{ps}$ in Nb (Ref. 13)). As mentioned earlier, this results from the rapid thermalization and subsequent diffusion of positrons to the grain boundaries. We note that the intensity I_1 of this lifetime component is more than 80% in all the samples. As discussed in the introduction, the thermal diffusion of positrons to the surface of grains smaller in size than their diffusion length would ensure a near-saturation trapping of positrons at the grain boundaries.

The intermediate lifetime τ_2 is significantly larger than that expected for annihilation events originating from the grain boundaries. There can be two interpretations for this, as it becomes conceptually difficult to perceive two distinctly different types of positron trapping centers localized in the same vicinity, i.e., the intercrystalline region. Qin *et al.* had suggested in their studies on nanocrystalline silver that the smaller lifetime τ_1 could result from positron annihilation in the vacancylike defects on the grain boundaries whereas the longer lifetime τ_2 could result from the trapping of positrons in microvoids (''vacancy-cluster defects'') at the intersection of two or more grain boundaries.[14] We presume that rather than the intersection of the boundaries, it is the extended nature of the intercrystalline region that enables positrons to enhance their lifetimes (τ_2) to 340–400 ps, as observed here. In fact, a small fraction of the positrons trapped in the extended intercrystalline regions can even form positronium (Ps) and annihilate after a long lifetime. We attribute the longer lifetime component $\tau_3 = 2.8\,\mathrm{ns}$ to the pick-off annihilation of ortho-Ps atoms formed in the intercrystalline region. In metallic systems, the formation of Ps is considered as a rare possibility. The present observation therefore is an added confirmation of the extended nature of the intercrystalline region characterized by a large free volume density.

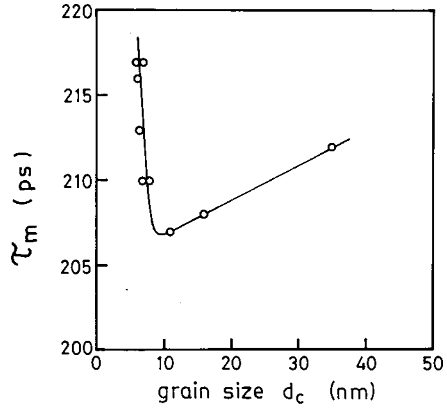

FIG. 4. The variation of the mean positron lifetime (τ_m) as a function of the grain size in nanocrystalline Nb.

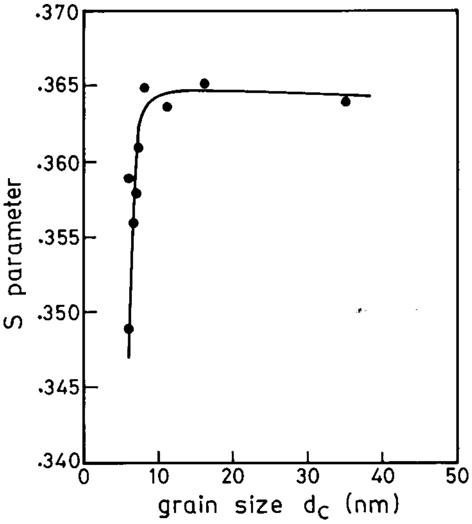

FIG. 5. The variation of S parameter with grain size in nanocrystalline Nb.

The material characteristics of nanocrystalline Nb appear to undergo significant changes below a grain size of about 10 nm (Figs. 3–5). All the positron annihilation parameters τ_1, τ_2, I_2, τ_m, and S show abrupt changes in their variation with grain size below 10 nm, as revealed in Figs. 3–5. The initial decrease of τ_1 (and of τ_2 during the grain-size reduction from 20 to 10 nm) with increasing time of ball milling (or decreasing grain size) is attributed to a possible contamination of the grain boundaries with Fe during milling in hardened steel vials and balls. However, as mentioned in our previous studies reporting the x-ray diffraction data analysis, the presence of Fe in negligible concentration can neither account for a polymorphic bcc→fcc transformation nor the accompanying lattice expansion.[1]

Both τ_1 and τ_2 abruptly start increasing as the grain size falls below about 10 nm. The decrease of I_2 in this particular context indicates a rise in I_1, which is the intensity of the lifetime τ_I. I_1 will increase when the annihilation probability at the grain boundaries will increase. And this happens as an increasing concentration of grain boundaries are being created while the grain size is reduced to smaller sizes.

For example, a grain-size reduction by half (which is more or less the case from 10 nm to the lowest size of 6 nm used in the present experiments), will increase the net grain-boundary area by ~26%. Second, we note that the intercrystalline regions are the least-packed regions of the nanocrystalline sample and the atomic arrangement in these regions becomes less rigid on decreasing the grain size. In other words, the increasing softening of the intercrystalline region would lead to rapid migration and agglomeration of the defects. The sharp rise in τ_2 below the grain size of 10 nm is in fact a clear indication of the effect of intercrystalline defect agglomeration, as a consequence of which the corresponding intensity I_2 could simultaneously fall. We shall make a few additional comments in this regard later. On the other hand, it also appears while observing the rise in τ_1 that the nanocrystalline grain boundaries get excess free volume below this grain size. While such a conjecture is always in agreement with a universal observation of an increasing positron lifetime with reducing grain size,[15,16] it needs to be validated by complementary experimental support or theoretical modeling. As positron annihilation is the most versatile experimental probe for studying the open-volume defects in solids, the evidence obtained in the present work stands out superior to other analytical observations and hence we shall try to work out a mathematical formulation of the excess free volume of atoms at the grain boundaries in nanocrystalline solids.

Phillpot, Wolf, and Gleiter[17] have shown that the atoms at the boundaries of nanocrystalline grains could be randomly displaced from their regular atomic sites to the maximum extent of 50% of the nearest-neighbor distance. Furthermore, the atomic structure of grain boundaries virtually lack long-range periodicity parallel to the interface. The atoms in the grain boundary will enjoy one additional degree of freedom of migration along the boundary plane than those in the bulk crystal.[18] Hence the excess free volume ΔV_F associated with the atoms of the grain boundaries may be conceived to have been confined to the plane parallel to the boundary region rather than being randomly distributed. With this approximation, the geometry of a grain can be described as a sphere of diameter equal to the grain size d_c inscribed in the tetrakaidecahedron geometry of a given nanocrystalline grain (Fig. 6).[19] The atom is considered to be located at the mean position (broken lines in the figure) of the interfacial region shared by two individual grains (thick solid line in the figure). Therefore ΔV_F can be considered equal in magnitude to the fractional excess surface area of the grain-boundary plane located at a distance of $(d_c+\Delta/2)/2$ from the center of a grain, where Δ ($=1$ nm) is the thickness of the grain-boundary plane assumed to be independent of d_c.[20] Thus the dimensionless value of ΔV_F can be expressed as

$$\Delta V_F=\frac{(d_c+\Delta/2)^2-d_c^2}{d_c^2}. \tag{3}$$

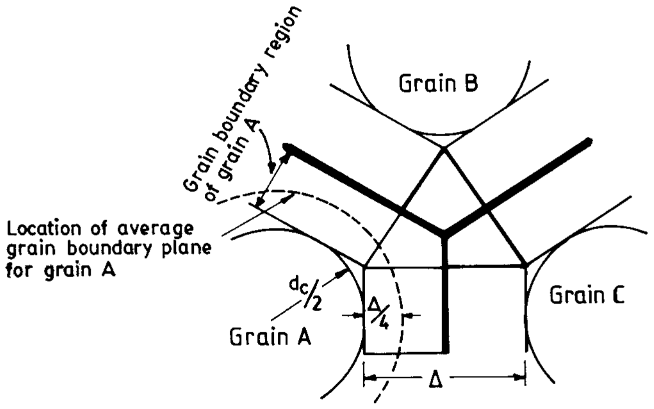

FIG. 6. Schematic description of the triple point junction formed by three adjoining tetrakaidecahedral grains *A*, *B*, and *C* (from Ref. 19). Superimposed on it are the approximated spherical geometry of the grains and the location of the average grain-boundary plane of *A*.

Figure 7 shows the variation of ΔV_F as a function of d_c obtained from the above equation. It is clear that the excess free volume of atoms does not change significantly with decreasing grain size until about 10 nm. Below this size, ΔV_F exhibits a sharp increase with grain-size reduction and becomes almost independent of d_c below 5 nm. Fecht had earlier predicted a value of $\Delta V_F=0.44$ [or $d_c=2.5$ nm from Eq. (3)] for the mechanical instability to set in while decreasing the grain size.[21] Moreover, a limiting grain size of around 1.5–2 nm had been predicted from the simulation of phonon density of states for the thermodynamic stability of nanocrystals.[22,23] As illustrated earlier in Fig. 2, the grain size decreases at a faster rate during the initial stages of ball milling and gradually attains a saturation level after about 20 h of milling. However, the region of occurrence of major changes in the free volume at the grain boundaries interestingly coincides with that at which significant changes of positron lifetimes and the *S* parameter are observed in Figs. 3–5.

The polymorphic transformation of Nb during the ball milling that we pointed out to occur from the observation of the diffraction lines in Fig. 1 should have brought in a closer repacking of atoms in the grain and hence a net increase of

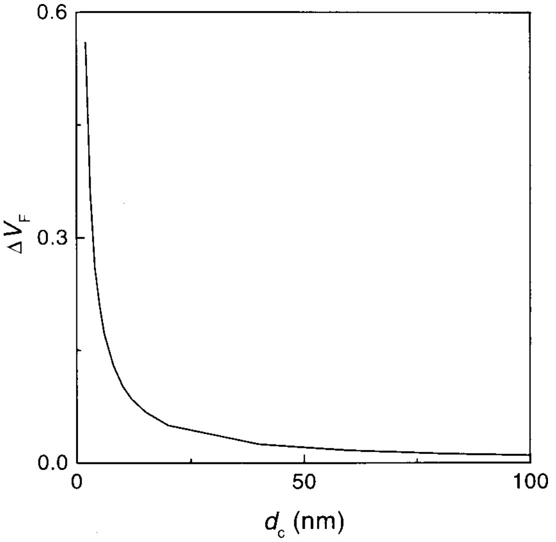

FIG. 7. Variation of the excess free volume (ΔV_F) of the atoms at the grain boundaries as a function of the grain size (d_c).

the packing fraction from 68 to 74 %. This effect however is nullified, if not overruled, by the concomitant lattice expansion that results in a 6% increase in volume per atom determined from the respective lattice parameters (i.e., 0.343 nm in the bcc phase and 0.428 nm in the fcc phase). The continued reduction in grain size, however, increases the free volume at the grain boundaries that results in a steep rise of positron lifetime, as shown in Figs. 3 and 4 and consistent with the results reported in earlier studies.[15,16]

There is still considerable ambiguity in the sharp reduction of the *S* parameter below the grain size of about 10 nm (Fig. 5). Normally in bulk metals, the positron lifetime and *S* are expected to indicate more or less identical qualitative variations as both are sensitive to the changes in the open-volume defect size and concentration. An instance of mutually opposite changes is seen in the work of Kizuka *et al.*,[24] where the authors have spoken about a probable enhancement in (quasi)-*Ps*-formation leading to a substantial increase in the *S* parameter. In the present case, the *Ps*-formation probability is negligibly small (less than 1%) and whatever trend that was available from the data analysis was a slight increase with decreasing grain size below 10 nm. But the *S* parameter sharply decreases in this grain-size regime. We note that the phase transformation from the bcc to fcc phase of the nanocrystalline grains brings in from the interior of the grains one additional atom per face of each unit cell forming the outermost atomic layer and hence the positrons trapped on the grain boundaries might locally encounter a situation identical to a transforming lattice with increased number of nearest-neighbor atoms with nearly unaltering distance (0.297 nm in bcc and 0.303 nm in fcc phases). The resulting redistribution of the average electron momenta might lead to the drastic reduction in *S*.

The processes and/or effects that will lead to such an atomic rearrangement on the grain boundaries or intercrystalline regions can be treated in more detail by looking at the residual compressive stress on the grain boundary on account of a lattice expansion taking place simultaneously with a reduction in grain size. We shall discuss some of these aspects in detail, owing to a need to reexamine the importance of grain-size reduction on the mechanical stability of the grain boundaries. An increase in ΔV_F with a reduction of the grain size will develop a negative hydrostatic pressure P_h at the grain boundary. As stated by Fecht,[21] the isothermal equation of state for a grain boundary is expressed as

$$P_h = -\frac{3B_0[(V/V_0)^{1/3}-1]}{(V/V_0)^{2/3}}\exp(-a^*) \times[1-0.15a^*+0.05(a^*)^2], \tag{4}$$

where B_0 is the equilibrium bulk modulus and V_0 is the equilibrium volume of the atom with equilibrium Weigner-Seitz cell radius r_{wse}. The quantity a^* is defined as $(r_{ws}-r_{wse})/l$, where r_{ws} is the real Weigner-Seitz cell radius of the atom with a volume V and l is the length scale characteristic of the metal.[21] The volume-dependent bulk modulus is defined as $B=-V(dP_h/dV)$ and its (as well as of $-P_h$) variation with ΔV_F (or the grain size d_c) is shown in Fig. 8. It should be noted that $-P_h$ is the magnitude of the hydrostatic stress corresponding to the negative pressure originating due to the excess free volume in the grain boundary as given in Eq. (3). From Fig. 8, we see that $-P_h$ increases rapidly below a grain size of 10 nm and levels off at very low grain sizes. The bulk modulus B varies directly with grain size and decreases very sharply below $d_c = 10$ nm (Fig. 8). It thus appears that the mechanical stability of the grain boundary decreases as the free volume per atom increases.

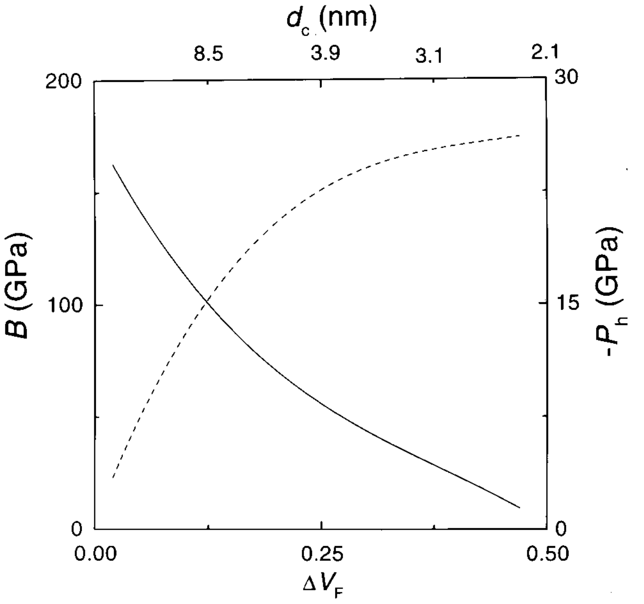

FIG. 8. Variation of the bulk modulus B (solid line) and the negative hydrostatic pressure $-P_h$ (broken line) as functions of the excess free volume ΔV_F and the grain size d_c.

The variation of $-P_h$ as a function of grain size may be treated in the following way to identify the genesis of the bcc to fcc transformation in Nb. A value of $-P_h$ (=20 GPa) obtained from Fig. 8 at the minimum value of d_c (~6 nm) obtained by ball milling of bcc Nb or in turn a value of $\Delta V_F = 0.16$ corresponds to a lattice expansion of 3.7%,[1] which is in close agreement with the experimentally determined value of 4% obtained in the present study (from Fig. 1). In addition, the amount of energy involved in such expansion (0.27 eV/atom[1]) is only slightly different from that predicted earlier for bcc to fcc transformation of Nb (0.09 eV/atom[25]). Further it could be noted that the combined effect of a decreasing grain size and an increasing fractional free volume at the grain boundaries would suggest an increase in free energy of the grain according to the Gibbs-Thomson equation $\Delta G = 4\gamma V_m d_c^{-1}$, where γ is the interfacial energy and V_m is the molar volume. The immediate consequence of such an increase in free energy would then be a phase transformation to counter the effect so that the structural stability can be retained. In other words, the decreasing grain size and the concomitant lattice expansion of bcc Nb may be considered responsible for bringing instability in the lattice of bcc Nb, which subsequently transforms into fcc Nb through a positive change in enthalpy.[25]

It may be noted that, as stated before, such a transformation is associated with a change in the number of atoms from four (for bcc Nb) to five (for fcc Nb) per face of the unit cell

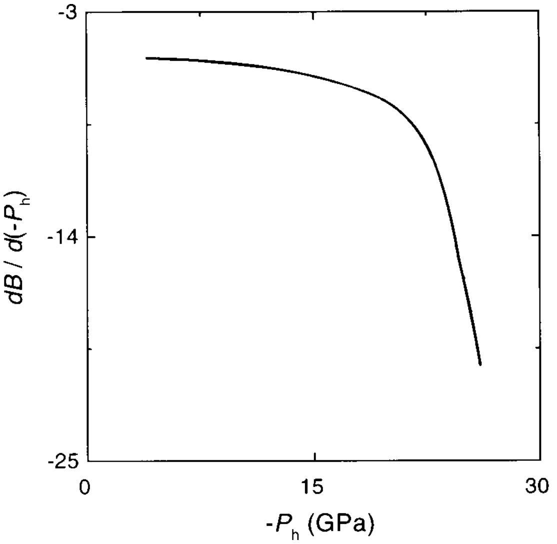

FIG. 9. The variation of $dB/d(-P_h)$ as a function of $-P_h$ for nanocrystalline Nb.

on the grain boundaries. This will necessitate a considerable amount of atomic rearrangement, and hence, sufficient atomic mobility at the grain surface. In this regard, a look at the change of $dB/d(-P_h)$ versus $-P_h$ (Fig. 9) shows it approaching infinity beyond a certain limit. Equations (3) and (4) predict a value of $\Delta V_F=0.24$ or $d_c=4$ nm for the onset of such a steep decline in $dB/d(-P_h)$ versus $-P_h$ curve. Thus, the result presented in Fig. 9 provides the theoretical argument for the occurrence of softening in the grain boundary, which is conducive for the predicted enhancement of atomic mobility at the grain boundaries. It may be recorded here that on extrapolation of $-P_h=0$ (i.e., equilibrium value in bulk Nb), $dB/d(-P_h)$ attains a value of 5.18, which is in reasonable agreement with $dB/d(-P_h)=4.72$ reported in the literature.[26] Such a description of grain-boundary softening and consequent atomic rearrangement in the near grain surface region associated with the lattice expansion and phase transformation will actually describe the steep fall in the S vs d_c curve (Fig. 5). On the other hand, the increase in τ_1 can be attributed to the effect of the increase in free volume of atoms on the grain boundaries, which possibly has only indirect linkage with the processes of lattice expansion and/or phase transformation, as already mentioned.

With a reduction in grain size below a certain size, say $\sim$10 nm in the present case, the value of $dB/d(-P_h)$ reveals a sharp reduction (Figs. 8 and 9). Such a trend will imply that the sliding of grain boundaries is the preferred operating mechanism for instabilities rather than the local pinning of defects. The motion of the atoms in the intercrystalline region is then comparable to that of a fluid between two slabs,[18] and consequently results in the migration and agglomeration of the intercrystalline defects. This further corroborates our argument for an independent reduction of the intensity I_2.

As the minimum grain size used in the present investigation is close to 5 nm, it is important to explore the likelihood of the occurrence of quantum size effects or discretization of energy levels in nanocrystalline Nb. From the theory of Wood and Ashcroft,[27] it can be shown that the quantization of bulk energy bands into discrete energy levels should take place when the grain size is reduced to a value given by the following equation:

$$d_c=\left[\frac{3\varepsilon_F}{\pi k_B T}\right]^{1/3} a, \tag{5}$$

where ε_F is the Fermi energy of Nb ($=5.32$ eV) and a is the lattice constant. The equation predicts a grain size of 1.9 nm for the energy-level splitting to take place at room temperature. The polymorphic transformation of bcc Nb to the fcc phase would only slightly shift it to 2.0 nm. Obviously both these grain sizes are below the limit of the mechanical and thermodynamic stability of the grain boundaries, whereas quantum confinement phenomena for grains of size about 5 nm may be observed at very low temperatures, say below 20 K.

V. CONCLUSIONS

We conclude from the above discussion that the polymorphic bcc→fcc phase transformation in nanocrystalline Nb following high-energy ball milling is a result of a remarkable reordering of the atoms on the grain boundaries and in the intercrystalline regions. This reordering is perhaps being prompted by a nearly collapsing rigidity of the grain boundaries and a characteristic lattice expansion within the grains. The abrupt changes in the positron annihilation parameters point to a drastic deviation from the microcrystalline properties as the grain size gets reduced to the true nanometric regime (typically below 10 nm). While the positron lifetime increases with decreasing grain size due to the increase in the excess free volume available at the grain boundaries, the Doppler broadened lineshape parameter decreased due to a net electron momentum redistribution resulting from the phase transformation and a concomitant lattice expansion. Interestingly, the model-based calculations of the bulk modulus and negative hydrostatic pressure on the grain boundaries also confirm the occurrence of both mechanical and thermodynamic instabilities of the grain boundaries below this size limit.

It should be mentioned that the increasing excess free volume being made available to the atoms of the outermost layer of the grains while decreasing the size of the latter is at the cost of mechanical stability of the grain boundaries and it can be a lower limit for the synthesis of stable nanoparticles.

We further rule out the possibility of discretization of electron energy levels or quantum size effects at room temperature as the expected grain-size regime for its occurrence is below the limit of mechanical stability of the grain boundaries. In this context, future investigations may be directed to explore its occurrence at very low temperatures ($T<20$ K).

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[*] Email address: cmoh99@yahoo.com
[†] Corresponding author. Email address: gopal@anp.saha.ernet.in
[‡] Email address: skpabi@metal.iitkgp.ernet.in
[§] Email address: imanna@metal.iitkgp.ernet.in

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