

Phonon density of states in nanocrystalline ^{57}Fe

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Abstract. The Born–von Karman model is used to calculate phonon density of states (DOS) of nanocrystalline bcc Fe. It is found that there is an anisotropic stiffening in the interatomic force constants and hence there is shrinking in the nearest-neighbour distances in the nanophase. This leads to additional vibrational modes above the bulk phonons near the bottom of the phonon band. It is found that the high energy phonon modes of nanophase Fe are the surface modes. The calculated phonon DOS closely agree with the experimental data except a peak at 37 meV. The calculated phonon dispersion relations are also compared with those of the bulk phonons and anomalous behaviour is discussed in detail. The specific heat in nanophase enhances as compared to bulk phase at low temperatures and the calculated Debye temperature Θ_D agrees with the experimental results. It is predicted that the nanocrystalline Fe may consist of about 14 GPa pressure.

Keywords. Nanocrystalline ^{57}Fe ; phonon DOS; Born–von Karman model; specific heat.

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1. Introduction

Over the past decade there has been much interest in the nanocrystalline materials due to their unusual elastic, electronic and magnetic properties [1,2]. The neutron inelastic scattering [3–7] and resonant inelastic nuclear γ -ray scattering [8] measurements have shown that there is an enhancement in the vibrational density of states at low frequencies as compared to bulk phonons and there is an overall shift of high frequency band beyond the top of the bulk phonons. The phonon DOS at low energies (below 15 meV) of nanocrystalline bcc ^{57}Fe is approximately quadratic in energy [8] and the phonon peaks also get broadened in the nanocrystalline phase. Trap *et al* [9] suggested that atoms at the grain boundaries have lower coordination number and hence softer force field as compared to bulk.

Kara and Rahman [10] did the cluster calculations using the interaction potential based on the embedded atom model [11] to investigate the dynamics of nanocrystals of Ag, Cu and Ni and found that there is an enhancement in the phonon DOS at low frequencies and an overall shift in the high frequency band beyond the top of bulk phonons. The vibrational density of states of surface atoms scales linearly with frequency at low frequencies. Meyer *et al* [12] studied the distribution of pressure in Ag, Cu and Ni nanocrystals with size in the range of 2 to 10 nm through molecular dynamics simulations. It is found that in the interior of the clusters large capillary pressure is built up and the surface tension derived

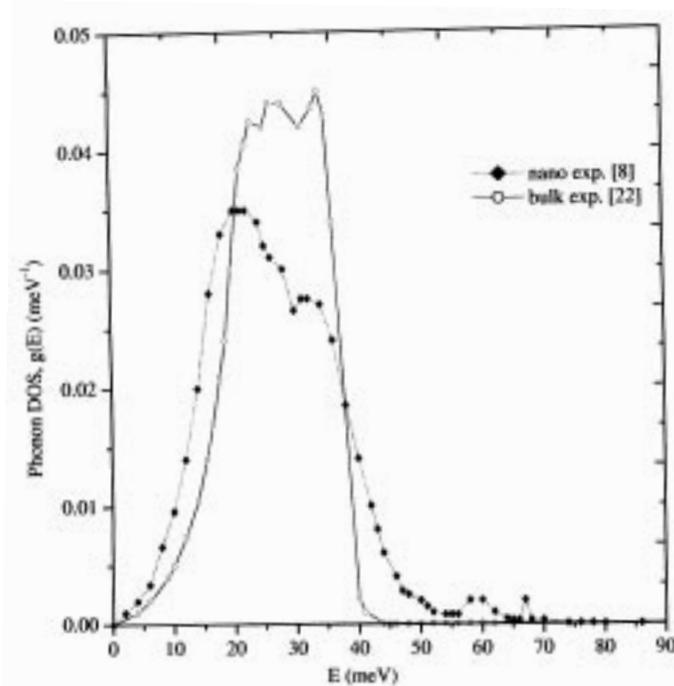


Figure 1. The comparison of experimental phonon DOS, $g(E)$ of nanocrystalline bcc ^{57}Fe with those of the bulk bcc Fe.

from the pressure is in good agreement with the macroscopic experimental data. Similar results were obtained by Swaminarayanan *et al* [13] also. The local vibrational density of states of cluster core is shifted towards higher frequencies. However, a comprehensive understanding of the origin of additional low frequency modes and high frequency tail of DOS in nanophase Fe metal is still awaited.

In this paper we have made an attempt to analyze the phonon DOS of nanophase bcc ^{57}Fe (10 ± 1 nm) in different energy ranges using Born–von Karman theory. The vibrational properties of nanoparticles, however, depend strongly on their size (see e.g. [14]) but here we calculated only the interatomic force constants of a sample of nanocrystalline ^{57}Fe (10 ± 1 nm) by fitting the calculated phonon DOS with those of experimentally reported [8]. Three-dimensional bcc lattice model is used for low and intermediate phonon energies and two-dimensional square lattice model for surface phonon modes. It is shown that the proportionality of DOS with energy square (E^2) near the bottom of the band is due to anisotropic stiffening of the force constants and high energy phonon tail is due to surface modes. The calculations are given in §2 and the results are discussed in §3.

2. Calculations

The experimentally reported phonon DOS for nanocrystalline and bulk bcc Fe are given in figure 1. Fultz *et al* [8] have shown through X-ray diffraction measurements that the ballis-

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Table 1. Interatomic force constants for bulk, nanointerior and (001) nanosurface of bcc Fe (in 10^4 dyne/cm).

Force constants	Bulk [15]	Nanointerior	Nanosurface
1XX	1.6280	1.6820	9.2620
1XY	1.4850	1.5020	0.0000
2XX	1.5520	2.4960	8.2520
2YY	0.0540	0.0864	8.2520
2XY	0.0000	0.0000	6.1078
3XX	0.1180	0.1260	
3ZZ	-0.0880	-0.8640	
3XY	0.1270	0.1410	
4XX	-0.0230	-0.0946	
4YY	0.0240	0.0460	
4YZ	0.0370	-0.9860	
4XZ	0.0070	0.0360	
5XX	-0.0460	-0.0986	
5XY	-0.0300	-0.3560	

tically consolidated nanocrystalline ^{57}Fe retains the bcc structure and its size is $10(\pm 1)$ nm. There are small thin disordered regions between the crystallites. In view of this experimental fact we assume that crystal symmetry of nanophase ^{57}Fe is bcc and use 5 nearest-neighbour (5NN) Born-von Karman (BvK) model to calculate its vibrational properties. The BvK model depends only on the nearest neighbours considered and is independent of the total number of atoms in the crystallite. Therefore, the structure of nanophase ^{57}Fe need not be optimised. The force constants for the bulk bcc Fe [15] are the initial input data. The boundary effects are accounted for by changing the force constants of distant NNs and including the surface modes.

Gilat and Raubenheimer's numerical integration method [16] is used to calculate the phonon density of states. The force constants are varied to get a close fit of the experimental data of phonon DOS in the low energy region. This is done by changing first the force constants of 1st and 2nd NNs and then the force constants of 3rd, 4th and 5th NNs. The close fit is obtained only when the force constants for the distant NNs were changed significantly as compared to that of the 1st and 2nd NNs. The same set of force constants is used to calculate the phonon dispersion relations and the phonon DOS for the intermediate energy region. Since we assume that crystal symmetry of nanophase and bulk phase single crystal to be the same, we compare these force constants and phonon dispersion relations with those of bulk phase single crystal [15] in table 1 and in figure 2 respectively. The complete calculations of phonon DOS of nanophase are compared with the experimental data in figure 3a. The phonon DOS has a sharp peak at about 37 meV and cut off at 44 meV.

The observed DOS for nanophase is spread up to 87 meV with small peaks at 60 and 68 meV. These energies are much above the bulk phonon region. Since the ratio of the number of surface atoms to volume atoms is large in the nanophase, it was realised that these phonons in the nanophase may be the surface modes. We used two-dimensional 2NN Born-von Karman model for the square lattice to calculate the phonon dispersion relation

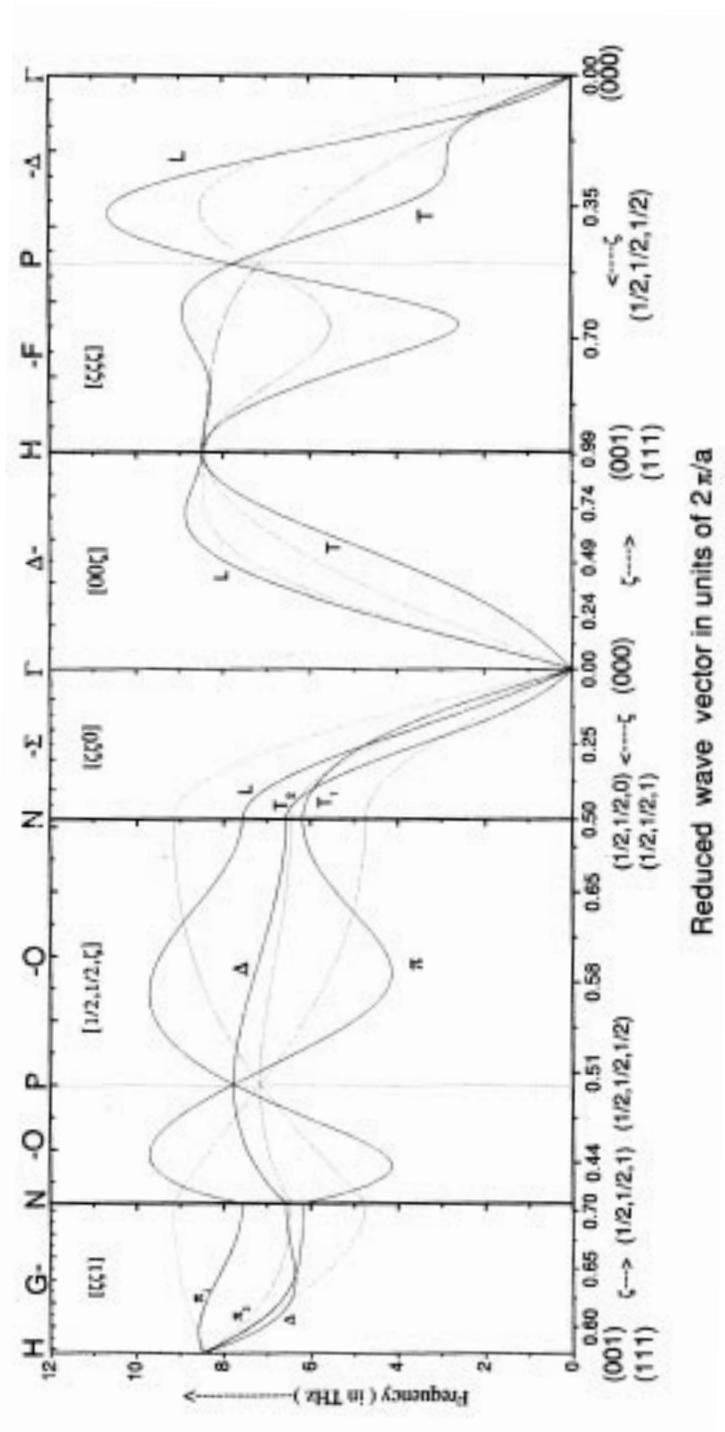


Figure 2. The phonon dispersion relations of nanocrystalline bcc⁵⁷Fe (solid lines) and bulk bcc Fe (dotted lines) along the symmetry directions.

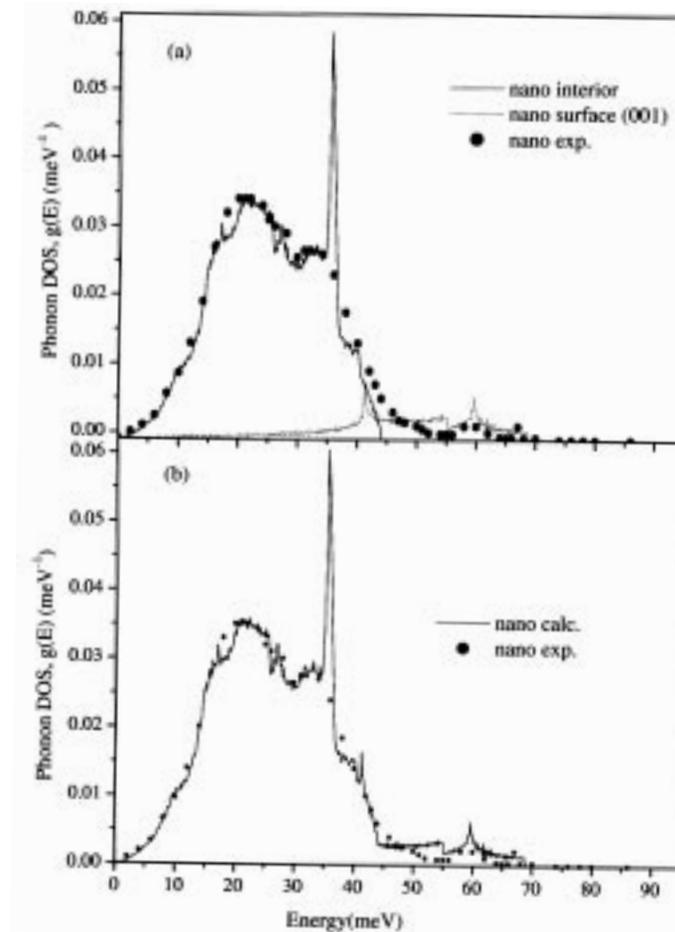


Figure 3. (a) Calculated phonon DOS, $g(E)$ of nanointerior and nanosurface (001) and experimental phonon DOS for nanocrystalline ^{57}Fe . (b) Total phonon DOS (nanointerior plus nanosurface) and experimental phonon DOS of nanocrystalline ^{57}Fe .

and phonon DOS of surface modes. The force constants are varied to match the peak in the phonon DOS at 60 meV in the experimental data. These force constants are also given in table 1 and the calculated phonon dispersion relations along the symmetry directions are compared with the calculations of Bortolani *et al* [17] for (001) surface of bulk Fe in figure 4. The calculated phonon DOS of nanointerior and nanosurface of nanocrystalline ^{57}Fe are compared in figure 3a. The total phonon DOS of nanophase is obtained by summing up these two contributions and these results are compared with the experimental data in figure 3b. The peak in phonon DOS at 37 meV continue to persist.

The total phonon DOS which includes both nanointerior and nanosurface is used to calculate the temperature dependence of specific heat and Debye θ_D of nanocrystalline Fe. These results are compared with those of bulk phase in figure 5.

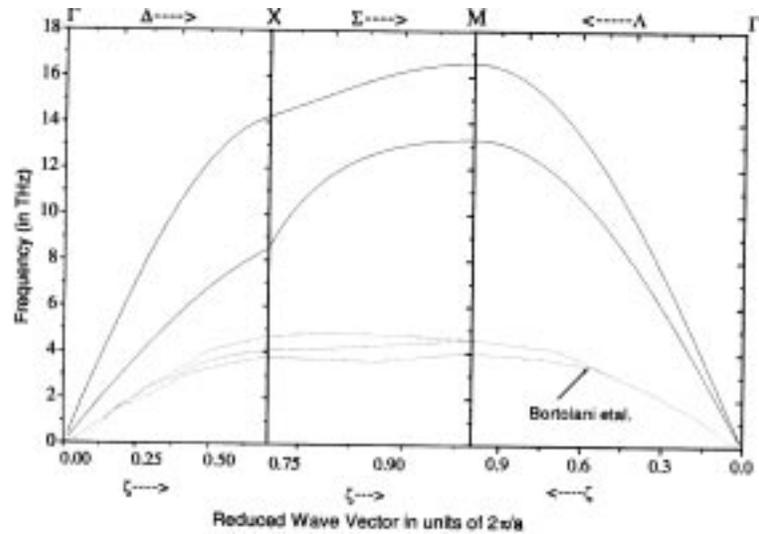


Figure 4. Phonon dispersion relations for surface modes of (001) surface of nanocrystalline Fe (solid lines) and bulk Fe (dotted lines).

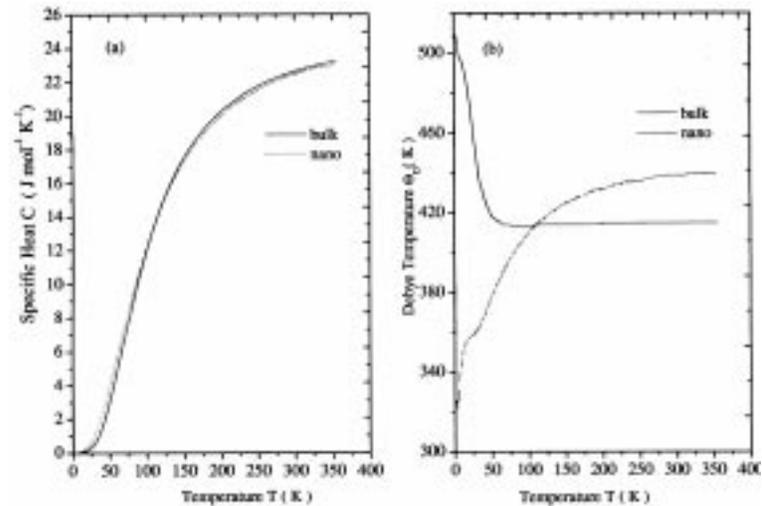


Figure 5. (a) Temperature dependence of specific heat, C and (b) Debye temperature $\Theta_D(T)$.

3. Discussion

The Born–von Karman model (up to 5th, 6th and even 8th) has been extensively used to determine the crystal lattice force constants for a long time. In this model the force constants are treated as fitting variables and the fit is done with the experimentally determined

phonon frequencies at few k-points. These force constants are used to calculate other vibrational and thermodynamic properties of the crystal. Here we did a little bit differently that the force constants are fitted to experimentally determine phonon DOS for the sample of nanocrystalline bcc ^{57}Fe [8].

It is evident from table 1 that the 1NN force constants of the bulk and nanophase Fe are nearly the same. However, the magnitude of the force constants of the nanophase increases as compared to that of the bulk phase beyond 2NN. At the 4NN, the magnitude of force constants of nanophase is two to three times that of the bulk phase and the sign of 4YZ force constant also changes. 5XY force constant is nearly ten times that of the bulk phase. Since the data of the bulk and nanophase are analyzed in the same model, it is concluded that the distant boundaries of nanophase Fe got anisotropically shrunk. This aspect is further confirmed by comparing the surface force constants, which are nearly two orders of magnitude more than the 5NN force constants of the bulk. Thus the surface atoms are exerting enormous pressure to retain the shape of nanophase material and there is an anisotropic shrinkage in the interatomic distances in the vicinity of the surface and on the surface of the nanoparticles. Feibelman [18] calculations show that the bond length of the dimer Fe in nanophase is 18.6% shorter than the NN distance of bulk Fe and there is contraction in the interplaner separation. Sokolov *et al* [19] have also shown that the Fe(310) surface is contracted by 16% and Fe(210) surface by 22%. Kara and Rahman [10] also predicted the shrinking in the NN distance in nanoclusters of Ag, Cu, and Ni and large capillary pressure has been shown by Meyer *et al* [12] and Swaminarayanan *et al* [13].

The phonon dispersion relations of the nanophase of ^{57}Fe are compared with those of the bulk phase single crystal in figure 2. There is an anisotropic change in the phonon frequencies in nanophase as compared to bulk phase. The phonon dispersion relations are anomalous in the nanophase. Along [111] direction, there is a cross over in the longitudinal (L) and transverse (T) branches at reduced wave vector $\zeta = 0.1$ and T branch is nearly flat at $\zeta = 0.25$. The longitudinal modes show a strong maximum at $\zeta = 0.4$ and deep minimum at $\zeta = 0.68$. Along [100] direction, the phonon frequencies of T modes are lower and L modes are higher than those of the bulk Fe. In the [110] direction the L, T_1 and T_2 modes cross over while such anomalous behaviour does not exist in the bulk phase bcc Fe. In the off-symmetry direction NP, the frequencies are out of the bulk phonon band while in the HN direction, these are in the bulk phonon band. These phonon anomalies may change the electron-phonon interaction and hence the transport properties.

The calculated phonon DOS agrees with the experimental data up to 40 meV as shown in figure 3a. However, there is a sharp peak at 37 meV which is found in the calculated results due to flatness of phonon dispersion relations in the transverse branch in the [111] direction at $\zeta = 0.25$ and near the zone boundary. Sturhahn *et al* [20] observed a sharp peak in phonon DOS in the vicinity of 40 meV in their experiments on α -Fe foil of thickness 10 μm by nuclear resonant fluorescent experiments. Molecular dynamics simulations [21] by Wassermann and Rieder have attributed the experimental peak of longitudinal optical modes in the high frequency region in MgO nanocrystals to surface inward relaxation. The molecular dynamics results of Meyer *et al* [12] also show a sharp change in pressure near the surface region. Therefore, the peak in the phonon DOS at 37 meV may be an indication of the existence of larger forces in the vicinity of surface of the nanocrystalline ^{57}Fe .

According to Lübbbers *et al* [22] as one moves from α -Fe phase to ϵ -Fe phase, one finds that DOS is shifted to higher energies with respect to α -Fe. The resolved high energy maximum of the DOS, originating mainly from LA (α -Fe) and LA and LO (ϵ -Fe) phonon

branches is shifted from 35 meV in α -Fe at ambient pressure to 51 meV in ϵ -Fe at 42 GPa. These observed changes reflect primarily the reduced volume of the unit cell.

The stiffening of the force constants has led to an enhancement in the phonon density of states at low energies and decrease in the phonon DOS at intermediate energies. Fultz *et al* [8] also made an attempt to fit the experimental data of phonon DOS by assuming the nanocrystalline Fe as the damped harmonic oscillator by assigning finite lifetime to phonons. Their model explained the high energy tail of phonon DOS, however their results deviated significantly in the low and intermediate energy up to 40 meV. Therefore, the anharmonic model of nanophase Fe was found insufficient to explain the phonon DOS.

The comparison of phonon dispersion relations for (001) surface of nanocrystalline Fe with those due to Bortolani *et al* [17] for (001) surface of bulk Fe in figure 4 shows that the general characteristics of the two dispersion relations are the same. However, the surface modes of the nanophase are nearly three to four times more energetic than the surface modes of the bulk phase. The phonon bandwidth is greatly enhanced. From figure 4, it is evident that the calculated surface modes are spread up to 69 meV and there are peaks at 41 and 60 meV which is again an indication of structural changes in the vicinity of the surface. As shown in figure 3b the calculated results closely agree with the experimental data except a sharp peak at 37 meV which needs further experimental investigations. It is concluded that the higher energy phonon modes are due to surface vibrations. Similar conclusions have also been drawn by Meyer *et al* [12] through their molecular dynamics simulations of Ag, Au, Cu and Ni nanoparticles. More recent MD simulations [21] by Wassermann and Rieder have attributed the experimental peak of longitudinal optical modes in the high frequency region in MgO nanocrystals to surface inward relaxation. Their calculations show varieties of relaxation shapes for clusters, shedding light on the contradictory data on nanocrystals and infinite surfaces.

It is interesting to compare our results with those due to Kara and Rahman [10]. Their calculations are real space calculations for the clusters of 225, 459 and 1289 atoms using the embedded atom potential for metals with the fcc structures. It is too difficult to account for exact dynamics of the surface atoms in these calculations. However, these authors conclude that higher energy phonons are due to contributions of inner atoms and low energy phonons due to surface atoms. Here we would emphasize to point out that the structure of real space clusters may be different from that of the actual nanophase particles on which the experiment has been performed. Moreover, the dynamics of nanophase bcc structure may be different from that of the fcc structured clusters. Here we have analyzed the experimental data of phonon DOS for bcc ^{57}Fe in the established Born–von Karman model for three- and two-dimensional systems and found that low energy additional phonons are due to compressed interior of nanoparticle and high energy phonons due to surface vibrations. Therefore our interpretation of low energy and high energy phonons does differ from the predictions of Kara and Rahman [10]. However, our conclusions are similar to those carried out by Meyer *et al* [12]. Therefore, more detailed experimental data on these metallic nanoclusters is needed to clarify these facts.

We find from figure 5 that there is a substantial increase in specific heat for the nanophase than the bulk phase up to 110 K. However, at higher temperatures the results for bulk and nanophase are nearly the same. It has been found that as compared to polycrystalline Pd and Cu, the specific heat for nanophase enhances nearly 10 to 50% [23]. Here it is to be noted that finer mesh integration gives $\Theta_D(T=0) = 508$ K as compared to earlier calculation of 467 K for the bulk phase. Our calculations show that $\Theta_D(T=0) = 384$ K

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for nanophase while the Mössbauer data analysis gives 345 K [24]. The difference may be due to calculational procedure. The $\Theta_D(T)$ for nanophase is smaller than that for bulk phase below 110 K and has a sharp minimum at about 2.67 K.

The average sound velocity calculated by Lübbbers *et al* [22] for Fe is 3.57 km/s (at 0 GPa), 4.82 km/s (at 20 GPa), 5.00 km/s (at 32 GPa) and 5.14 km/s (at 42 GPa). In our calculations for nanophase ^{57}Fe the average sound velocity is found to be 4.442 km/s. The pressure in the nanophase can be roughly estimated from the bulk data given above. The linear interpolation of data shows that the nanophase ^{57}Fe is at nearly 14 GPa of pressure which is of the same order as calculated by Meyer *et al* [12].

4. Conclusions

The calculated phonon DOS agrees closely with the experimental results. It is found that there is an anisotropic stiffening in the interatomic force constants and hence there is shrinking in the nearest-neighbour distances in the nanophase. It is concluded that the low energy additional phonons arise due to compressed interior of nanoparticle and high energy phonon modes arise due to surface vibrations and the nanophase may consist of about 14 GPa pressure. The importance of the present calculations is that the force constants determined by analyzing the experimental data for phonon DOS of nanocrystalline bcc ^{57}Fe can be used to calculate its other vibrational and thermodynamic properties. In the present work these have been used to calculate its phonon dispersion relations, specific heat and Debye temperature.

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