

Moessbauer recoilless fractions in nanocrystals

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Lattice vibrations in a nanocrystalline solid, in contrast to bulk crystalline solid, will have an additional contribution from surface scattering. Mean square displacement (msd) of atoms in a nanocrystal is calculated using such an additional contribution. The zero-point vibrational correction to the msd is found to vary as the inverse square of a nanocrystal size (L). Furthermore, the temperature dependent term of the msd is found to vary as $\exp(-1/TLk)$, where k is a constant. Since a structural distortion of a nanocrystalline solid can be expected to set in, at a particular temperature, we introduce a gap in phonon dispersion. Calculations of the Lamb-Moessbauer (LM) factors with a gap in dispersion show that $f(T)$ shows a global maximum at a threshold temperature (T_{th}). Thermal expansion is expected to occur at $T < T_{th}$, while thermal contraction should result at $T > T_{th}$ with increasing T . The gap is the result of a size dependent phonon scattering. We compare calculated $f(T)$ and thermal expansion with measured results of these observables on nanometer-sized Au particles.

I. INTRODUCTION

Recently there has been a lot of interest in nanocrystals as nanosize particles embedded in a matrix and as independent particles in a powder. In some problems, one starts with the known nanocrystal size and calculates the adsorption energies or any other physical property. In other problems, the physical properties are first measured and from that the nanocrystal size is determined. The understanding of the physical properties of the nanocrystals is very important because of their application in the device fabrication. In the modern times, the components are often of the size of a few microns. If these components can be made within the size of a few nm, there will be a gain of a factor of 10^3 . The much smaller currents can perform the same function which was previously performed by much larger currents. We have calculated the Moessbauer recoilless fraction for a fractal [1-3] and for a superconducting lattice [4,5]. For nuclei in a solid, when the γ ray is emitted, a large fraction is recoilless. This fraction depends on the lattice dynamics through the root mean square displacement of an atom, $[\langle u^2 \rangle]^{1/2}$. The recoilless fraction is given by $\exp(-\langle u^2 \rangle / \lambda^2)$ where λ is the wave length of the emitted γ ray. We have calculated [6-9] the effect of lattice vibrations on the isomer shift which has been observed [10,12].

In this paper, we calculate the mean-square displacement of an atom in a nanocrystal due to scattering of phonons of wave length of the order of the size of the nanocrystal. The recoilless fraction is nontrivial because of two terms with different slopes so that there is apparent "thermal contraction".

II. THEORY

We consider that the material consists of an ensemble of nanocrystals. The size of the nanograin is d . The sound waves are scattered by the nanograin if the distance between two sides of a grain is an integer multiple of the wave length. In the case of x-rays, the diffraction is determined by the Bragg's law. The distance between atoms is of the order of the wave length, λ , so that the scattering occurs at, $2d \sin \theta = n\lambda$, where θ is the angle which the incident ray makes from the normal to the surface parallel to which the next atomic layer is located at a distance, d , from the first surface and n is an integer. We consider the sound waves or phonons in the solid which are scattered by the surface boundaries of the nanocrystals. The wave length of the phonons or that of the sound waves is, $\lambda = v/\nu$, where v is the sound velocity and ν is the frequency of the lattice wave. The phonon frequency which is scattered by the nanograin is, $\omega = 2\pi\nu/2d \sin \theta$. The lower value of the phonon frequency is obtained by taking $\sin \theta = 1$ as, $\omega_1 = \pi\nu/d$ where v is the sound velocity, $v \approx 5 \times 10^5$ cm/s. For the frequency of $\nu = 10^{12}$ Hz, we get 5π nm for the particle size. The high frequency can be cutoff by replacing $\sin \theta$ by an average value, $\langle \sin \theta \rangle = 1/2$ so that the upper cutoff frequency becomes, $\omega_2 = 2\pi\nu/d$. Thus we have determined the range of frequencies introduced by the nanocrystal in addition to the usual phonon frequency spectrum in the bulk crystal. This type of phonon scattering within the nanocrystal may be called the "phonon confinement". The effect of such a scattering is to produce a particle size dependence in the specific heat [13].

In a harmonic oscillator, the displacement of an atom is given by,

$$\delta R = (\hbar/2M\omega_k)^{1/2}(a_k + a_{-k}^\dagger) \quad (1)$$

so that the phonon correlation factor becomes $(2n+1)$ which gives the zero-point as well as the temperature dependent terms in the mean-square displacement (msd). Using the Debye cutoff frequency, we find,

$$\begin{aligned} \langle u^2 \rangle = & 3\hbar\omega_D^2/(16\pi^2\rho v^3) \\ & + (3\hbar/2\pi^2\rho v^3)(k_B T/\hbar)^2 \int_0^X x(e^x-1)^{-1} dx \end{aligned} \quad (2)$$

where ρ is the mass density. Therefore, the msd varies as T^2 at low temperatures in a three dimensional solid. In the case of scattering from the boundaries the msd for a nanocrystal is given by,

$$\langle u^2 \rangle_{\text{nano}}(0) = [3\hbar/(8\pi^2\rho_n v_n^3)](\omega_2^2 - \omega_1^2). \quad (3)$$

We substitute the values of the two limiting frequencies from the above to obtain,

$$\langle u^2 \rangle_{\text{nano}}(0) = 9\hbar/(8\rho_n v_n d^2). \quad (4)$$

Therefore, for $v = v_n$, the above expression shows that the mean-square displacement of atoms is proportional to the inverse square of the nanoparticle size, d . The largest term in the temperature dependent contribution, added to the above expression gives the msd in the form,

$$\langle u^2 \rangle_{\text{nano}}(0) + \langle u^2 \rangle_{\text{nano}}(T) = a_1/d^2 + a_2(T/d)\exp\{-a_3/(Td)\} \quad (5)$$

where $a_1 = 9\hbar/8\rho_n v_n$, $a_2 = 3k_B v/2\pi\rho_n v_n^3$ and $a_3 = \hbar\pi v/k_B$. This msd varies as $1/d^2$ at low temperatures and then there is a term of the form of $(T/d)\exp(-a_3/Td)$. Thus the particle size plays an important role at low temperatures. At high temperature, $x \ll 1$, so that the integral can be simplified and the msd becomes,

$$\langle u^2 \rangle_{\text{nano}}(0) + \langle u^2 \rangle_{\text{nano}}(T) = a_1/d^2 + a_4(T/d) \quad (6)$$

where $a_4 \approx 3k_B/2\pi\rho_n v_n^2$. Thus, the msd varies as $1/d^2$ and there is a temperature dependent term which varies as $1/d$. If there is a gap in the phonon dispersion, ω_1 works like a gap corresponding to lattice distortion at this frequency.

III. MELTING POINT

We use Lindemann criterion to determine the melting temperature of a nanocrystal. It is assumed that the lattice melts when,

$$\langle u^2 \rangle = ca_o^2 \quad (7)$$

where a_o is the usual lattice constant and $c \approx 0.1$. We apply Eq. (7) to Eq. (6) so that by ignoring the quantum mechanical zero-point term, we obtain the melting point as,

$$T_{nm} = 0.1a_o^2 d/a_4 \quad (8)$$

which means that the larger crystals have larger melting temperatures. Let us consider the zero-point contribution also. Then, by using the Lindemann criterion we obtain,

$$ca_o^2 - (a_1/d^2) = (a_4/d)T_{nm} \quad (9)$$

for the melting temperature of a nanocrystal. Now the value of T_{nm} is slightly reduced compared with the value given by Eq. (8). Whereas T_{nm} versus d is linear in Eq. (8), in Eq. (9) it is slightly bent from the linear behavior. This kind of linear dependence as well as bending predicted here from the surface scattering is in accord with the melting found experimentally in Si, Bi and CdS.

IV. RECOILLESS FRACTION

The recoilless fraction is written as $f = \exp(-4\pi^2\langle u^2 \rangle/\lambda^2)$ where λ is the wave length of the γ ray. The recoilless fraction in a nanocrystal is given by,

$$f = \exp[-4\pi^2(\langle u^2 \rangle + \langle u^2 \rangle_{\text{nano}})/\lambda^2] \quad (10)$$

which can be written as,

$$f = f_c f_n \quad (11)$$

where f_c is the value in a crystal and f_n in a nanocrystal. From Eq. (8) the above can be written as,

$$f = f_c f_n(0) f_n(T). \quad (12)$$

When the frequency increases by means of extra scattering at the surface of the nanocrystal, we expect u^2 to increase compared with that in the crystal but the interpretation is nontrivial. The mass density in a nanocrystal is slightly smaller than in the bulk crystal. It is like a "negative pressure" in going from the bulk solid to a nanocrystal. In the study of specific heat it has been shown that there are new modes due to nanometer size of the particles. The application of this mode gives the correct interpretation of recoilless fraction in Au. Usually, the recoilless fraction is as given above Eq. (10), and the mean-square displacement is $u^2 = (\hbar/2M\omega)(2n+1)$. Considering only the $n = 0$ term, the msd becomes $u^2(0) = (\hbar/2M\omega)$. The mode found in the nanocrystal has the frequency of $\omega = \pi v/d$. Substituting this value of the frequency in the mean square deviation gives $u^2(0) = (\hbar d/2M\pi v)$. The recoilless fraction now depends on d , the size of the crystal as,

$$f = \exp(-4\pi^2\hbar d/2M\pi v\lambda^2). \quad (13)$$

In this expression, smaller particles have larger f . This prediction is in agreement with the experimental observation of recoilless fraction in Au. This means that the vibrations at the frequency $\pi v/d$ play a dominant role in nanocrystals than the usual phonon continuum.

Thermal expansion. Usually a material expands due to anharmonic forces in the solid. The size of the unit cell is measured by using x-ray diffraction or a high resolution microscope as a function of temperature. As the temperature is increased, the unit cell expands. In the nanocrystals, there is a vibrational mode which depends on the size, d , of the crystal. The frequency of this mode is predicted to be about $\pi v/d$. It is of interest to study the effect of excitation of this mode on the unit cell size. As the system is warmed, at a particular temperature, the size dependent mode acquires sufficient population to dominate over the usual phonon continuum. Therefore, the thermal expansion of the unit cell switches from the phonon continuum to the size-dependent mode. This type of switching occurs at a particular temperature which may be called the “switching temperature” and hence detectable by x-ray measurements. We assume that there is no kinetic energy and hence the potential energy is given by,

$$U(x) = cx^2 - gx^3 - fx^4. \quad (14)$$

We suppose that the thermal expansion arises from the gx^3 type anharmonicity and ignore the fx^4 type anharmonicity. The cx^2 is the usual harmonic potential. The thermal expansion is determined by,

$$\langle x \rangle = \int dx x \exp(-\beta U) / \int dx \exp(-\beta U) \quad (15)$$

where $\beta = 1/k_B T$. We assume that cx^2 is much larger than x^3 and x^4 type terms so that,

$$\langle x \rangle_{\text{bulk}} = (3g/4c^2)k_B T \quad (16)$$

which increases with increasing anharmonicity and reduces by increasing harmonic force constant. As the temperature is increased, the harmonic force in the frequency domain is described by $c = m\omega^2/2$ with frequency $\omega = \pi v/d$ where v is the sound velocity and d is the size of the nanocrystal,

$$\langle x \rangle = 3gk_B T / (m^2 \omega^4). \quad (17)$$

If the nanograins are spherical, it is sufficient to use only one value of ω so that the above expression gives,

$$\langle x \rangle_{\text{nano}} = 3gd^4 k_B T / (\pi^4 v^4 m^2) \quad (18)$$

which varies as d^4 . As the temperature is increased the thermal expansion switches from $\langle x \rangle_{\text{bulk}}$ to $\langle x \rangle_{\text{nano}}$ so that there is a peak in $\langle x \rangle(T)$. At low temperatures $\langle x \rangle$

expands with increasing T with slope given by $\langle x \rangle_{\text{bulk}}$. At a particular temperature the surface mode becomes important and the slope of $\langle x \rangle_{\text{bulk}}$ becomes irrelevant and then the slope is determined by $\langle x \rangle_{\text{nano}}$. This means that dx/dT has a positive sign at low temperatures as well as at high temperatures but in the intermediate range of temperatures, it has negative sign so that there is “thermal contraction” in addition to “thermal expansion” at low and high temperatures. This thermal contraction is characteristic of the nanocrystals. This predicted behavior agrees with experimental observation of thermal contraction in Au nanoparticles.

V. EXPERIMENTAL DATA

^{196}Pt is irradiated by neutrons to produce ^{197}Pt from which the neutron decay produces ^{197}Au which gives 77 keV γ ray with a half life of 18 h. The Moessbauer measurements of this γ ray have been performed by Marshall and Wilenzick [14] and more recently by Vieger and Trooster [15]. From these measurements it is obvious that smaller particles have larger recoilless fraction as predicted by Eq. (13). The thermal expansion of Au particles of size 4 nm has been measured by Li *et al.* [16]. The cell parameter is about 0.4067 nm at zero temperature. As the temperature is increased, it expands to 0.4081 nm at 125 K but it reduces as the temperature is further increased becoming about 0.4054 at 400 K. This kind of thermal “contraction” can arise from two mechanisms of expansion if the system switches from one mechanism to another. Therefore, the data is consistent with the theory. It means that below 125 K usual phonon anharmonicity gives the thermal expansion but above this temperature the phonon mode with size dependent frequency becomes important.

VI. CONCLUSIONS

We conclude that there are new phonon modes in nanocrystals which are related to the scattering at the surface. At low temperatures the usual lattice dynamics determines the lattice properties but at a particular temperature the system switches from the bulk dynamics to the surface dynamics. Therefore, the recoilless fraction is dominated by the particle size. Similarly, the thermal expansion is determined by the anharmonicity but above a particular temperature, switches to that from the surface anharmonicity which depends on the particle size. Similarly the coordination also changes as a function of pressure [17].

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