

Change in low-temperature thermodynamic functions of a semiconductor due to a quantum dot

V. K. Tewary

Materials Reliability Division, National Institute of Standards & Technology, Boulder, Colorado 80305

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A phonon Green's function method is developed for modeling the phonon modes of a semiconductor perturbed by a quantum dot. Simple expressions are derived for the frequency spectrum of perturbed low-frequency phonon modes and changes in the Helmholtz-free energy and the constant-volume specific heat at low temperatures using the Debye model. The changes are found to be significant and can be used to characterize the material properties of the quantum dot. The theory is also applicable to nanocrystals and other nano-inclusions in solids.

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I. INTRODUCTION

We show that a quantum dot (QD) causes significant changes in the phonon spectrum and the low-temperature thermodynamic functions of the host semiconductor. These changes can be measured which can provide useful parameters for characterizing the material properties (elastic constants, density) of the QD. Knowledge of these parameters is necessary for modeling the formation, growth, and stability of QD's and their arrays. Characterization of QD's is needed because the material parameters for a QD are, in general, different than those for the bulk solid. Our results suggest a new method of characterizing QD's which would supplement the information obtained by the present methods such as those based upon photoluminescence, Raman spectroscopy etc.

We develop a Green's function method for modeling phonons in solids containing QD's. We define a defect phonon Green's function that gives the frequency-dependent response of a solid containing a defect such as a QD. It accounts for the fact that the material parameters of the QD are different from the host solid. The Green's function is useful for the calculation of the thermodynamic functions and other phonon-related characteristics of the solid such as the Debye-Waller factor. Our method is an adaptation of the powerful discrete lattice Green's function method¹⁻³ that has been used successfully for modeling crystal lattices with point defects.

In addition to modeling the phonons, our method can be used for the calculation of stresses and strains associated with a QD since the elastostatic response of a solid is simply given by the zero-frequency limit of the phonon Green's function.² The use of the defect phonon Green's function method is new in the continuum mechanics modeling of QD's. The earlier Green's function method for QD's⁴⁻⁶ is limited to elastostatic calculations and does not account for the difference between the material parameters of a QD and the host solid. The importance of the difference between the elastic constants of the QD and the host solid has recently been discussed in detail by Ellaway and Faux.⁷

We use the Green's function to calculate the change in the frequency spectrum of the host solid and its thermodynamic functions caused by the presence of a QD. Our objective is to obtain an order of magnitude estimate of the above changes

and to illustrate the use of our defect phonon Green's function method. For low-temperature thermodynamic calculations the simple Debye model is adequate¹ which is valid at low frequencies. Here "low temperatures" refer to temperatures T which are much less than the Debye temperature when the Debye T^3 law is obeyed. Similarly, "low frequencies" refer to frequencies $\omega \ll \omega_D$, the Debye cut-off frequency. In the Debye model, a solid is treated as an isotropic scalar continuum. For elastostatic calculations and more detailed calculations of phonon characteristics, the full tensor form of the Christoffel equations has to be used.

When an impurity is introduced into a solid, it perturbs the phonon modes¹ of the host solid. If the impurity has internal degrees of freedom such as a QD, it also has internal and interfacial phonon modes. Thus the total phonon modes of a solid containing a QD consists of internal modes of the QD modified by the host solid, interfacial modes, and the modes of the host solid perturbed by the impurity. The internal and interfacial modes of a QD have been studied in considerable detail by many authors [see, for example, Refs. 8, 9]. However, a study of the perturbed low-frequency modes or change in the low-temperature thermodynamic quantities of a solid due to these modes has not been reported in the literature. Our interest in this paper is in these low-frequency phonon modes of the host solid perturbed by the presence of a QD.

The internal and interfacial modes of QD's⁸⁻¹⁰ are relatively high-frequency modes that can be observed by techniques such as Raman spectroscopy.^{11,12} They do not significantly affect the low-temperature thermodynamic quantities because the contribution of a phonon of frequency ω at temperature T is weighted by the factor $\exp(-\hbar\omega/k_B T)$ where \hbar is Planck's constant and k_B is the Boltzmann constant. Further, the frequency spectrum of these modes may have a linear dependence on ω . Some modes may be isolated and localized.¹ Their frequency spectrum has a delta-function dependence on ω as in the Einstein model. These modes do not give the T^3 dependence of C_v , the specific heat of the host solid at constant volume at low temperatures.^{13,14} The frequency spectrum of a perfect solid (without QD's) is proportional to ω^2 that gives the T^3 dependence of the specific heat as $T \rightarrow 0$.

On the other hand, we find that the frequency spectrum of the perturbed low-frequency phonon modes has the quadratic

and higher-order dependence on ω . The quadratic term is of the same order as in the perfect Debye solid. Phonons in the Debye model are nondispersive. The presence of higher-order terms in the frequency spectrum shows the dispersive behavior of phonons induced by the presence of a QD. Further, the perturbed low-frequency phonon modes change the low-temperature thermodynamic quantities of the host solid. The quadratic and the higher-order terms in the frequency spectrum change the coefficients of T^3 and higher-order terms in the T dependence of C_v . This changes the effective Debye temperature of the host solid as well as its temperature dependence. Their measurements can give useful information about the elastic constants and the density of the QD, which should supplement the information obtained by measurements on relatively higher-frequency phonon modes.

We have applied our theory to QD's in InAs/GaAs and Ge/Si. The change in the specific heat is proportional to the volume concentration of QD's and depends upon the elastic constants and density of the host solid and the QD. Our formulation is also applicable to nanocrystals or other nanoinclusions in solids. We hope that these calculations will encourage detailed measurements on changes in the thermodynamic functions due to the formation of QD's and nanocrystals.

II. PHONON GREEN'S FUNCTION FOR THE DEBYE MODEL

The Debye model can be derived by taking the scalar form of the Christoffel equations of elastic equilibrium, which is

$$(\partial/\partial x_j)[E^*(x)(\partial/\partial x_j)]u(x) + \rho^*(x)\omega^2 u(x) = F(x), \quad (1)$$

where x is the 3D position vector, $j=1, 2, \text{ or } 3$ denotes a Cartesian component, $F(x)$ is the applied force, $u(x)$ is the displacement field, E is an effective elastic constant in the Debye approximation, and ρ is the density of the solid. To account for inhomogeneities in the solid due to the presence of a QD, E^* and ρ^* are shown in Eq. (1) as functions of x . The summation convention over repeated indices is assumed.

We assume that a single QD is located at $x=0$ within an area enclosed by the surface S . The elastic constant and the density of the material forming the QD are assumed to be $E - \Delta E$ and $\rho - \Delta\rho$, respectively, where E and ρ are the corresponding parameters of the host solid without inclusions. We can write

$$E^*(x) = E - H(S-x)\Delta E, \quad (2)$$

$$\rho^*(x) = \rho - H(S-x)\Delta\rho, \quad (3)$$

where H is the step function for vector arguments, and is 1 if x is contained within S , and is 0 otherwise.

Using Eqs. (2) and (3), the solution of Eq. (1) in matrix notation is given by¹

$$u = G^* F^*, \quad (4)$$

where

$$G^* = [L^*]^{-1}, \quad (5)$$

$$L^* = L - H(S-x)\Delta L, \quad (6)$$

$$L = E\nabla_x^2 + \rho\omega^2, \quad (7)$$

$$\Delta L = \Delta E\nabla_x^2 + \Delta\rho\omega^2, \quad (8)$$

∇_x^2 is the Laplacian operating on x , and $F^*(x)$ includes the additional terms on the (LHS) left-hand side of Eq. (1) containing eigenstrains at the surface of the QD arising from the derivative of $H(S-x)$. Knowledge of F^* is not required for calculations of the phonon modes, which are determined by the LHS of Eq. (4). For notational brevity, we have not shown the functional dependence of various quantities on ω .

In Eq. (4) G^* is the defect Green's function for the solid. It is distinguished from $G = L^{-1}$, which is identified as the perfect Green's function of the solid without the defect term ΔL . The operators are represented in the vector space of the solid so we can write them in the form of matrices with their elements labeled by x and x' .

From Eq. (5), using the matrix notation

$$G^* = GT^{-1}, \quad (9)$$

where

$$T(x, x') = [\delta(x, x') - H(S-x)\Delta L_x G(x, x')]. \quad (10)$$

Equation (9) has the same structure as that for defects in lattices which has been studied extensively.¹⁻³ The vector space generated by all values of x in S defines the defect space. The second term on the RHS of Eq. (10) is nonvanishing only in the defect space. For localized defects, the dimensionality of the defect space is finite. We can therefore use the matrix partitioning technique¹⁻³ for calculating the defect Green's function. Using this technique,¹⁻² we obtain the following expression for the block of the T matrix defined by Eq. (10) in the defect space:

$$M(x, x') = \delta(x, x') - \Delta L_x G(x, x'), \quad (11)$$

where x and x' are both confined to the defect space where $H(S-x)=1$.

The defect Green's function as defined by Eq. (9) includes the effect of the change in the material parameters of the QD through the term ΔL . It gives a convenient formulation for calculating the change in the response of a solid due to the presence of a QD or any other nanoinclusion. Equation (4) gives the displacement field in the solid due to a QD in terms of the defect Green's function. The elastostatic field is obtained by taking the $\omega \rightarrow 0$ limit of the Green's function.² Our present interest is only in the phonon modes. These are given by the poles of the Green's function¹ and the frequency spectrum is given by the imaginary part of its diagonal element ($x=x'$).

As shown in Ref. 1, *all* the perturbed phonon frequencies are given by the zeroes of $D(\omega)$, the determinant of M . In order to calculate M , we first calculate G for the Debye model by using the Fourier representation of the Green's function as given below:

$$G(x, x') = -(1/\rho) \int (c^2 k^2 - \omega^2)^{-1} \exp[ik \cdot (x - x')] dk, \quad (12)$$

where the integration is over the Debye sphere in reciprocal space and $c^2 = E/\rho$. As in the Debye model, we take the volume per mode as equal to $1/V$, where $V = (4\pi/3)K^3$ is the volume of the Debye sphere and K its radius.

From Eqs. (8) and (12), the second term on the RHS of Eq. (11) is given by

$$\Delta L_x G(x, x') = (\Delta\rho/\rho) \int \gamma(k) \exp[ik \cdot (x - x')] dk, \quad (13)$$

where

$$\gamma(k) = (\eta^2 k^2 - \omega^2)(c^2 k^2 - \omega^2)^{-1} \quad (14)$$

and $\eta^2 = \Delta E/\Delta\rho$.

For simplicity, henceforth we neglect the size of the QD and assume it to be confined to a single-lattice site of volume $1/V$. This is a reasonable assumption because our interest is only in low-frequency phonons whose wavelengths are much larger than the size of the QD. In this approximation $x = x' = 0$ is the only element in Eq. (11) and $M = D(\omega)$ becomes a scalar.

In the integral in Eq. (12), we apply the branch cut at the negative real axis and introduce a vanishingly small imaginary part in the frequency¹ as $\omega = \omega - i0$. We then evaluate the integral over a sphere of radius K . From Eqs. (11) and (12), we obtain

$$D(\omega) = 1 - (\Delta E/E) [1 + 3d\xi^2 + (3d/2)\xi^3 \times \{\ln(1 - \xi)/(1 + \xi) - \pi i\}], \quad (15)$$

where $\xi = \omega/\omega_D$, $\omega_D = cK$ is the Debye frequency, and $d = 1 - c^2/\eta^2$.

III. CHANGE IN THE PHONON FREQUENCY SPECTRUM AND THE THERMODYNAMIC FUNCTIONS

In order to verify our model, we first show that the phonon Green's function defined by Eq. (12) gives the Debye frequency spectrum. We write $\omega^2 = \omega^2 - i0$ in Eq. (12) and calculate the diagonal part ($x' = x$) of the Green's function. After carrying out the integration over the Debye sphere of radius K , we obtain

$$G(x, x; \omega^2) = -(3V/\rho\omega_D^2) [1 + (\omega/2\omega_D) \times \{\ln(\omega_D - \omega)/(\omega_D + \omega) - \pi i\}]. \quad (16)$$

The frequency spectrum $g(\omega)$ is given by¹

$$g(\omega) = 2\omega(\rho/\pi V) \text{Im} G(x, x; \omega^2 - i0) = (3/\omega_D^3)\omega^2, \quad (17)$$

which is the Debye formula. The low-temperature specific heat corresponding to Eq. (17) per atom (or per mode) is given by¹

$$C_v(T) = k_B(4\pi^4/5)\beta^3, \quad (18)$$

where $\beta = T/\theta$ and $\theta = \hbar\omega_D/k_B$ is the Debye temperature. The change in the frequency spectrum¹ caused by a single QD is given by

$$\Delta g(\omega) = (1/\pi) \text{Im}(d/d\omega) \ln D(\omega). \quad (19)$$

If we expand the RHS of Eq. (19) at low frequencies, the first two terms are

$$\Delta g(\omega) = (3B/2)\xi^2 + (5B^2/2)\xi^4, \quad (20)$$

where

$$B = 3\Delta E d / (\Delta E - E). \quad (21)$$

From Eq. (20) we see that the leading term in $\Delta g(\omega)$ is of the same order as in $g(\omega)$. The ω^2 term in the frequency spectrum corresponds to nondispersive propagation of phonons as in the Debye model. The presence of higher-order terms in Eq. (20) shows dispersion of phonons caused by the QD.

The change in the frequency spectrum can be used to calculate the changes in thermodynamic and other functions of the solid that depend upon the frequency spectrum of phonons. However, it is possible to calculate the change in the thermodynamic functions directly by using Eq. (15) on the imaginary axis.¹ This gives the following change in the Helmholtz-free energy as $T \rightarrow 0$,

$$\Delta F(T) - \Delta F(0) = k_B T [(\pi^4/30)B\beta^3 - (4\pi^6/63)B^2\beta^5 + O(\beta^7)]. \quad (22)$$

The change in the constant-volume specific heat is given by

$$\Delta C_v(T) = -T\partial^2 \Delta F(T)/\partial T^2. \quad (23)$$

From Eqs. (22) and (23), we finally obtain

$$\Delta C_v(T) = -k_B [(4\pi^4/10)B\beta^3 + (40\pi^6/21)B^2\beta^5]. \quad (24)$$

We see from Eq. (24) that the presence of the QD changes the coefficients of the T^3 as well as higher-order terms. The change in the T^3 term would change the effective Debye temperature of the solid. The change in the T^6 term will change the temperature dependence of the Debye temperature. For low concentration of QD's the total change is proportional to the concentration.¹ Thus, from Eqs. (18) and (24), the fractional change in the lowest-order term is given by

$$\Delta C_v(T)/C_v(T) = -\varepsilon B/2, \quad (25)$$

where ε is the relative volume concentration of the QD's.

The change in the specific heat of the solid due to quantum dots can also be expressed in terms of an effective Debye temperature of the solid and its temperature dependence. From Eqs. (18), we write C_v^* , the total specific heat of the solid per degree of freedom, in terms of the effective Debye temperature θ^* as follows:

$$C_v^*(T) = C_v(T) + \Delta C_v(T) = k_B(4\pi^4/5)(T/\theta^*)^3. \quad (26)$$

From Eqs. (18), (25), and (26), we obtain the following expression for the effective Debye temperature of the solid containing low concentration of QD's and low temperatures:

$$\theta^*/\theta = 1 + \varepsilon B/6 + (50\varepsilon\pi^2/63)B^2(T/\theta)^2. \quad (27)$$

As an example, we consider InAs QD's in GaAs and Ge QD's in Si. The effective elastic constant in the Debye model of an anisotropic solid should be calculated by taking an appropriate average in different directions. In the present case, our objective is only to demonstrate the phonon Green's function method and apply it to qualitatively study the effect of the perturbed modes and obtain an order-of-magnitude estimate of the changes in the thermodynamic functions of the solid. We shall therefore make a simple and reasonable assumption that E is equal to the bulk modulus of the solid. The results are given below (E in 10^{11} Pa; ρ in 10^3 kg/m³): (i) InAs QD's in GaAs, $E(\text{InAs})=0.58$, $\rho(\text{InAs})=5.67$; $E(\text{GaAs})=0.76$, $\rho(\text{GaAs})=5.32$. This gives $B=1.2$ and $\Delta C_v(T)/C_v(T) \approx -0.6\varepsilon$. (ii) Ge QD's in Si, $E(\text{Ge})=0.75$, $\rho(\text{Ge})=5.32$; $E(\text{Si})=0.98$, $\rho(\text{Si})=2.33$. This gives $B=5.9$, and $\Delta C_v(T)/C_v(T) \approx -3\varepsilon$.

We see that, as physically expected, $\Delta C_v(T)$ is large if the difference between the material parameters of the QD and the host is large. Even for $\varepsilon=10^{-2}$, $\Delta C_v(T)$ is significant. In many actual cases ε may be much larger. For large concentrations, the interaction between the QD's will be important, which we have neglected. If the interaction between QD's is included, the result will depend upon higher powers of ε and will cause a stronger perturbation on the host modes. In view of rather crude approximations that are inherent in the Debye model, our results are essentially quali-

tative and provide only an order-of-magnitude estimate of $\Delta C_v(T)$ and $\Delta F(T)$. In general, the values of the elastic constant and the density of the material in a QD are different than those for the bulk. The above results show that measurement of $\Delta C_v(T)$ and $\Delta F(T)$ can provide an estimate of ΔE and $\Delta\rho$ for the QD.

IV. CONCLUSIONS

The phonon modes of a solid are perturbed by the presence of a QD or any other nanoinclusion. This is in addition to internal phonon modes of the QD itself and any interfacial modes. The frequency spectrum of the perturbed phonon modes is proportional to ω^2 in the lowest order and also contains higher-order terms. The presence of higher-order terms in the frequency spectrum shows dispersion of phonons. The perturbed phonon modes change the coefficient of the T^3 and higher-order terms in the low-temperature specific heat of the solid. This would result in a change in the Debye temperature as well as its temperature dependence. The change is proportional to the concentration of the QD's. A measurement of these changes can give useful information about the elastic constants and the density of the QD's. These parameters are needed for modeling the formation, growth, and stability of QD's and their arrays.

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