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Far-infrared spectroscopy of $Cd_{1-x}Mn_xS$ quantum dots

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ABSTRACT

Far-infrared reflectivity spectra, in spectral region 50–600 cm^{-1} and temperature region 80–300 K, of CdS and $Cd_{1-x}Mn_xS$ nanocrystals embedded in hexametaphosphate, are presented. The analysis of the far-infrared experimental reflectivity spectrum was made by the fitting procedure. The Maxwell–Garnet effective medium theory is used for modeling an effective dielectric function as well as to separate respond from nanoparticles.

To analyze spectra in CdS ω_{TO}(≈238 cm^{-1}) to ω_{LO}(≈305 cm^{-1}) spectral region, quantized dipolar modes in a spherical isotropic material quantum dot (QD) are considered in the framework of a continuum model. As to the mechanical boundary conditions rigid sphere is concerned. Experimental far-infrared reflectivity spectra of our samples are in general agreement with the predictions of this model.

Experimentally registered and through fitting procedure located features for CdS nanoparticles in spectral region below CdS ω_{TO} at: ≈102 cm^{-1}, ≈135 cm^{-1}, ≈170 cm^{-1} and ≈210 cm^{-1} are associated to defect induced modes, especially to defects located near the surface of CdS QD. In region over CdS ω_{LO}, modes are identified as multiphonons. In $Cd_{1-x}Mn_xS$ QD spectra new reflectivity peaks are at: ≈85 cm^{-1}, ≈110 cm^{-1} and ≈180 cm^{-1} in spectral region below CdS ω_{TO}, ≈270 cm^{-1} inside CdS ω_{TO}–ω_{LO} spectral region and ≈356 cm^{-1} and ≈376 cm^{-1} in region over CdS ω_{LO}. First two registered modes are associated to both mass and force constant defects at the surface, and rest four modes are consequence of MnS phases present in the sample.

1. Introduction

Vibrational spectroscopy (far-infrared and Raman) is a useful, non-destructive procedure sensitive to local environment, ideal for *in site* probing during growth, and during device fabrication and operation. In low-dimensional semiconductors optical phonon modes behave substantially different from those of bulk. Optical phonons confined in semiconductor QDs affect the electronic properties responsible for Raman scattering. Most of the experimental studies of optical phonons in QDs have been performed by Raman spectroscopy [1–5]. Quantum-size effect on optical phonons can also be seen by far-infrared (FIR) spectroscopy [6–10].

Diluted magnetic semiconductors (DMS) are alloys with magnetic ions diluted in nonmagnetic $A^{II}B^{VI}$ semiconductors. Mn^{2+} ions can be incorporated into an $A^{II}B^{VI}$ semiconductor host in large proportions without substantially altering the crystallographic quality of the material. Mn^{2+} has a relatively large magnetic moment due to the $3d^54s^2$ electronic configuration. Mn^{2+} is electrically neutral in an $A^{II}B^{VI}$ host, thus avoiding the formation of any acceptor or donor impurities in the crystal. In the nanometer-size, many of the physical properties of DMS are expected to be influenced by quantum confinement of the electronic states and hence differ from those of the bulk crystals. Magnetic properties of Mn^{2+} incorporated in CdS and ZnS nanoparticles are widely investigated [11,12]. Optical properties were studied, and fluorescence due to isolated Mn^{2+} ions in tetrahedral coordination was observed and attributed to a quantum size effect [13–15].

$Cd_{1-x}Mn_xS$ is DMS which belongs to a group of materials known as mixed crystals. Phonon spectra of mixed crystals depend of the properties of end members. It is known that CdS, end member in $Cd_{1-x}Mn_xS$ dominating in the case of small x, crystallize in wurtzite (as in our case) or sphalerite lattice structure. Bulk $Cd_{1-x}Mn_xS$ exists in wurtzite structure for x up to ~0.45 [16]. Vibrational spectra of pure CdS and mixed crystals with CdS as one end-member are well known [17]. Bulk CdS samples are very reflective between ω_{TO} = 240 cm^{-1} and ω_{LO} = 304 cm^{-1}, and flat with low reflectivity out of this region. Second end member, MnS appears in three crystallographic modifications [18]. One of them is α-MnS that crystallizes in the cubic structure of NaCl type. The TO(LO) frequencies of this phase are 185(330) cm^{-1} [19]. The zincblende crystallographic modification of MnS (β-MnS) has phonon frequencies of TO(LO) modes at 286(343) cm^{-1}. These phonon frequencies

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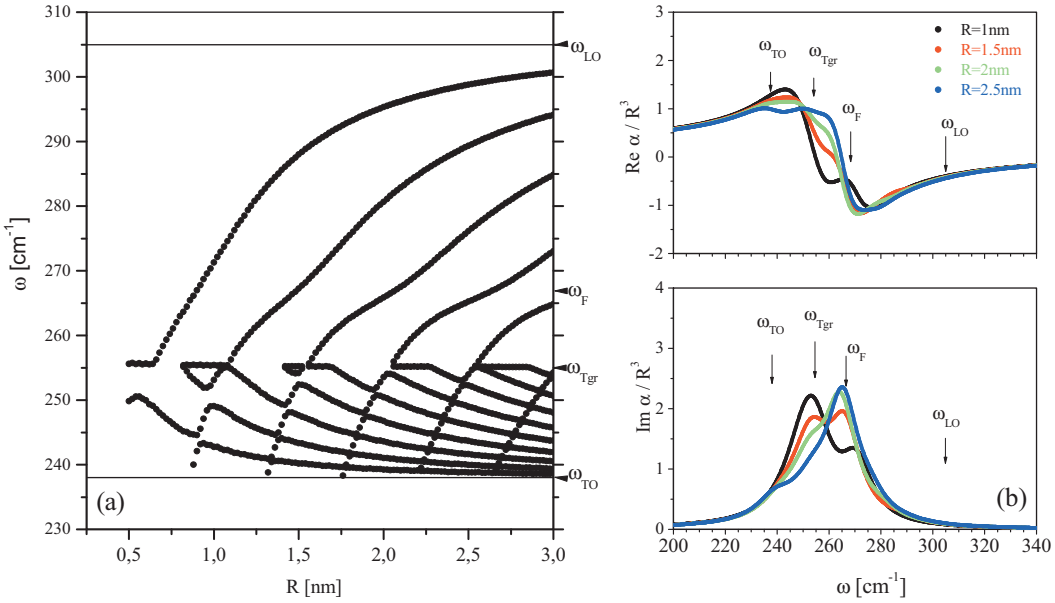

Fig. 1. (a) The radial dependence of $l = 1$ phonon frequencies calculated for CdS QDs (rigid boundary conditions) embedded in a matrix with $\varepsilon_2^\infty = 4$. The Fröhlich mode is at ≈267 cm^{-1}. (b) Real (up) and imaginary (down) parts of the polarizability for CdS spheres of different radii embedded in matrix with $\varepsilon_2^\infty = 4$.

were obtained from far-infrared reflectivity measurements of β-MnS thin films [20]. The phonon properties of zincblende MnS have been investigated in ZnS–MnS alloys [21]. Using the modified random element-isodisplacement (MREI) model, the TO(LO) mode frequencies of β-MnS were calculated at 293(361) cm^{-1}. Some investigations [22] show phonon frequency of zincblende MnS thick layers to be 380 cm^{-1}. The third modification of MnS is wurtzite MnS (γ-MnS), but this one is not of our interest here.

In studying vibrational modes of nanocrystals, knowledge of phonon dispersion of bulk material is required. For proper treatment of materials with dispersive phonons it is essential to satisfy mechanical as well as electromagnetic boundary conditions at the surface of particle. The group of authors [23] developed a theory for the optical vibrational modes of quantum dots (QDs) and showed that correct boundary conditions demand the coupling of longitudinal and transverse modes. The effect of correct mechanical boundary conditions is most significant to the smallest nanocrystals of materials with dissipative phonons.

In this paper we report results of experimental FIR reflectivity spectra of composites containing CdS and $Cd_{1-x}Mn_xS$ nanosize crystals. $Cd_{1-x}Mn_xS$ nanoparticles ($d \approx 4.5$ nm) of various compositions, $x = 0$, 0.01, 0.05, 0.1, 0.15, 0.3, were prepared by colloidal chemistry based procedure. We also presented results of theoretical studies of FIR active vibrations in spherical, nanosized CdS QDs. The phonon related polarizability of single CdS QD and effective dielectric function of composites containing QDs with narrow size distribution are calculated. The effects of QD dimension and volume fraction to effective dielectric function and consequently to reflectivity spectra, for this ideal case, are analyzed.

2. Synthesis and characterization of $Cd_{1-x}Mn_xS$ nanoparticles

Colloidal dispersions consisting of $Cd_{1-x}Mn_xS$ nanoparticles were prepared by mixing solution containing $Cd(NO_3)_2$ and $MnSO_4$ with solution containing Na_2S in the presence of surface active agent sodium hexametaphosphate $(NaPO_3)_6$. The concentration of cations ($[Cd^{2+}] + [Mn^{2+}]$) was constant and equal to 2×10^{-3} M, while an "excess" of S^{2-} ions was used in the synthesis (2.4×10^{-3} M). The content of Mn^{2+} ions was varied up to $x = 0.30$. The concentration of $(NaPO_3)_6$ was 2×10^{-2} M. The light and air were excluded during the preparation of colloidal dispersions. After precipitation of colloidal particles the solvent was removed by vacuum evaporation at room temperature. The obtained yellow powders could be redissolved in water to give a colloid with the same structured absorption spectrum as the solution before evaporation of the solvent. The contents of cations in powders consisting of $Cd_{1-x}Mn_xS$ nanoparticles were checked out by measuring atomic absorption (ICP-AS Perkin-Emer 6500). The X-ray diffraction analysis of $Cd_{1-x}Mn_xS$ nanoparticles performed for various compositions showed hexagonal wurtzite structure of CdS. UV–vis absorption spectra were recorded on Perkin-Elmer Lambda 5 instrument. A blue shift of the absorption onset of the CdS nanoparticles compared to bulk CdS was about 0.3 eV. The diameter of the particles was calculated using effective mass approximation model [24]. The calculated value for the diameter of CdS nanoparticles was found to be about 4.5 nm.

3. Quantized dipolar modes

A continuum model of the optical phonon confinement in a spherical QD treats properly both mechanical and electrostatic boundary conditions. This model, which uses parameters of bulk phonon dispersion curves, is limited to nanoparticles of regular shape made of bulk material. Although this is not the case in real nano-crystallites, we present results of calculation for ideal spherical CdS QD.

We assumed that particles are small spherical semiconductor crystals surrounded by matrix material. Materials are assumed to be isotropic and homogeneous, separated by the surface of the sphere. First, we considered one small spherical CdS crystal of radius R [25,26]. This consideration of confined optical vibrations in nanocrystals is based on macroscopic equation for the relative displacement ($\vec{u}$) of the positive and negative ions:

$$(\omega^2 - \omega_{TO}^2)\vec{u} = \beta_L^2 \vec{\nabla}(\vec{\nabla}\vec{u}) - \beta_T^2 \vec{\nabla} \times (\vec{\nabla} \times \vec{u}) + \frac{e_T \vec{\nabla}\varphi}{\rho v}. \quad (1)$$

The parameters of the equation are: ρ is the reduced mass density, ω_{TO} is the TO bulk frequency, $e_T = \sqrt{\varepsilon_1^\infty \mu v(\omega_{LO}^2 - \omega_{TO}^2)/(4\pi)}$ the transverse charge, v is the unit cell volume, and β_T and β_L