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Intrinsic Radiative Rates of Infrared-Emitting Germanium Nanocrystals

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Introduction
Germanium is an indirect gap semiconductor in the bulk and therefore, a poor light emitter. Its conduction band minimum and valence band maximum have different crystal momenta, leading to a radiative recombination process of charge carriers that requires the participation of a momentum-conserving phonon. However, this physical picture significantly changes at the nanoscale, where spatial confinement of carriers leads to a spreading of their wavefunctions in momentum space, making phononless direct-like radiative transitions possible. In this work, we explore the effects of quantum confinement on radiative recombination in the strong confinement regime (nanocrystal size significantly smaller than the exciton Bohr radius of 24 nm) by employing time-resolved photoluminescence (PL) spectroscopy at variable temperatures and magnetic fields.

Experimental
Colloidal germanium nanocrystals are synthesized by a solution-based method in which GeI₂ is used as a precursor. The resulting NCs are highly crystalline and have a size range of 3-4 nm with corresponding emission wavelengths of 0.9-1.2 μm and a maximum PL quantum yield of 8% [1]. In order to investigate the nature of these emitting states, we have performed time-resolved PL measurements as a function of temperature (1.7-300 K range) and magnetic field (0-15 T). The measurements were carried out in the variable-temperature inserts of both an 18 T and a 7 T superconducting magnet (Oxford Instruments) at NHMFL-Los Alamos.

Results and Discussion
PL dynamics indicate a significant confinement-induced enhancement of radiative lifetimes for Ge NCs (tens of microseconds) compared to bulk values (~0.5 s). The observed temperature- and magnetic field-dependence of the PL lifetimes point to the presence of an optically dark (dipole-forbidden) lowest excited state closely separated from an optically allowed bright state. Independent measurements of thermal activation of the bright state and magnetic-field-induced mixing of the dark and bright states (see Figure 1) yield a consistent energy scale of the splitting of about 1 meV. We further analyze our results by considering the magnitude of this splitting in comparison to the lowest acoustic phonon energies available for thermal activation and relaxation between the dark and bright states. These measurements are complementary to our recent studies [2] of nonradiative processes in germanium nanocrystals, where we have established that Auger recombination undergoes a transformation from a phonon-assisted (bulk) to a phononless (NCs) process, greatly enhancing rates compared to bulk and having the same V-scaling (Auger rates proportional to particle volume) as NCs of direct gap semiconductors.

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References