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Spontaneous magnetization and ferromagnetism in PbSe quantum dots

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A high-temperature organic solution approach was applied to prepare crystalline PbSe quantum dots. It is diamagnetic with an atomic susceptibility of $\sim -1.0 \times 10^{-4}$ emu/mol Oe for bulk PbSe. The core diamagnetism of bulk PbSe was subtracted from our raw data. While transforming into the nanophase, orbital susceptibility including finite-size corrections to the Landau susceptibility has been observed. A paramagnetic zero-field peak with a large diamagnetic susceptibility in high fields exhibit in the field dependent susceptibility as characteristics of the Landau orbital susceptibility. At low temperatures and fields the paramagnetism dominates the contribution of magnetization of quantum dots while the diamagnetism dominates at high temperatures and fields. All these measurements, showing paramagnetism at low fields, indicate the existence of spontaneous magnetization in the quantum dot. In addition, we have observed profound hysteresis loops implying ferromagnetism among the quantum dots even at room temperature, which is spontaneous magnetization in the quantum dot and of the ferromagnetic order among these quantum dots.

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Although physical properties, especially electronic and optical properties, of semiconductors at the nanometer scale have been studied extensively,¹ measurements of magnetic susceptibility have rarely been reported. In the early 1990s, Lévy *et al.*² measured magnetic susceptibility of an ensemble of isolated GaAs squares and found a large paramagnetic susceptibility at zero field. To remove magnetic response from the spin contributions, the authors used dc superconducting quantum interference device (SQUID) with ac fields and obtained the differential of susceptibility instead of measuring the magnetic susceptibility directly. They carried out measurements of the orbital susceptibility. As the size of the squares is small compared to the mean free path, the ballistic billiards will display orbital magnetism. In 2002, Schwarz *et al.*³ reported that the magnetization of electrons in semiconductor quantum dot (QD) array was lithographically inscribed on AlGaAs/GaAs heterostructure. The authors concluded that the electron–electron interaction strongly affects the magnetization of QDs with an average lateral size of 550 nm. Recently, Neeleshwar *et al.*⁴ studied size-dependent properties of CdSe QDs which were synthesized by a chemical method and were protected by some capping agents. They determined that the magnetic susceptibility changes to more positive value with a decrease of the QD size.

Many theoretical reports^{5–7} describe the Landau diamagnetism of free electron gas enclosed in a box of finite volume. They argued that finite-size corrections to the Landau susceptibility could properly explain the paramagnetic zero-field peak which was observed in Lévy's experiments.² In addition to the semiclassical approach, another method using an atomic picture to treat QDs was proposed to demonstrate the linear orbital response of the QDs.⁸ The orientational paramagnetism and precession diamagnetism, which were dependent on and independent of temperature, respectively, provided insights into the role of electron–electron interactions in the QD. Recently, Krasny *et al.*⁹ calculated both the orbital and the spin magnetic properties of QDs and showed a paramagnetic spin contribution at low temperatures and fields, and a diamagnetic orbital contribution at high temperatures and fields. Experiments on magnetic susceptibility of QDs have not been carried out in detail to examine the theoretical works mentioned above. In this article, we show the magnetization of PbSe QDs in comparison with theoretical works and report a ferromagnetism among the PbSe QDs.

PbSe QDs with different sizes were prepared by using a high-temperature organic solution approach.^{10–13} The sizes of QDs were selected post synthesis and the size distribution was monitored using a transmission electron microscope (TEM). The average diameters of two monodisperse PbSe QDs were determined as 10.5 and 6.7 nm on the basis of TEM images, whereas the standard deviations were calcu-

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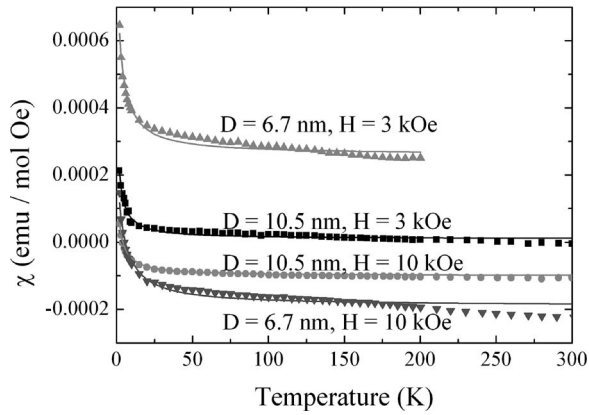


FIG. 1. Temperature dependence of magnetic susceptibility of PbSe quantum dots. The diameter (D) of PbSe quantum dots and the applied magnetic field (H) are labeled in the graph. Solid lines are Curie-Weiss fit of the data.

lated as 7.1% and 4.1%, respectively. The crystalline structure and the spherical shape of both sizes of PbSe QDs were observed on TEM as well. Magnetic properties of PbSe QDs were investigated using a SQUID magnetometer (Quantum Design MPMS-7), within a temperature range from 2 to 300 K and under a field from 0 to 50 kOe. The magnetization of PbSe QDs is at least ten times larger than that from a background noise of the sample holder which mainly contributes from the capsule, i.e., about -1×10^{-4} emu at 1 kOe.

The as-grown PbSe QDs stabilized by capping agents of both trioctylphosphine (TOP) and oleic acid. According to results of thermogravimetric analysis (TGA), the weight ratio between the organic compound and the PbSe is $\sim 10\%$ in both samples. The molecular susceptibilities from TOP and oleic acid are about -0.12 and -0.11×10^{-4} emu/mol Oe, which are smaller than the diamagnetic susceptibility of bulk PbSe (-1.0×10^{-4} emu/mol Oe)¹⁴ by ten times, and can be neglected. We only subtract the core diamagnetism of bulk PbSe from our raw data, and the resulted outcomes suggest a magnetic response from QDs.

The temperature dependence of magnetic susceptibility is presented in Fig. 1. All the curves of magnetic susceptibility as a function of temperature show a Curie paramagnetism at temperatures lower than 20 K (see a Curie-Weiss fit in Fig. 1). For QDs with the same size of 6.7 nm, the magnetic susceptibility exhibits paramagnetics-diamagnetic interplay with an increase of magnetic field. The observed paramagnetic and diamagnetic behaviors at low fields and at high fields, respectively, are consistent with theoretical calculation.⁹ By reducing the size of the QDs from 10 to 6.7 nm, the magnetic susceptibility, taken at a low field of 1 kOe, becomes more positive (paramagnetic); in contrast, the magnetic susceptibility is more negative (diamagnetic) when data from a high field of 10 kOe are chosen. The results of size dependence of low-field (1 kOe) susceptibility are in good agreement with a recent report of a study on CdSe QDs.⁴ In addition to a positive shift of magnetic susceptibility at a low field for the smaller QDs, we have realized a negative shift of susceptibility at a high magnetic field.

The magnetization of QDs at high temperatures is displayed as a function of magnetic field in Fig. 2. The magne-

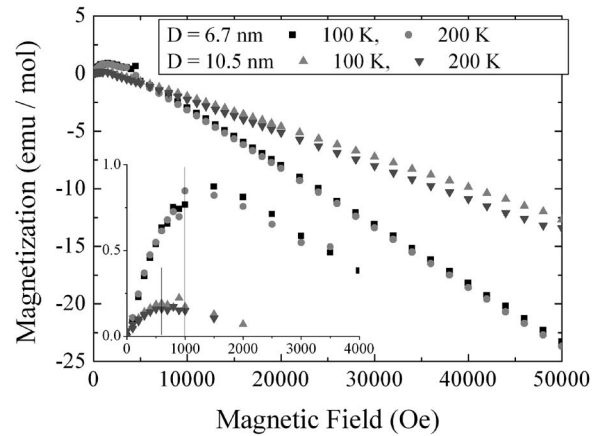


FIG. 2. Magnetization as a function of magnetic field taken at 100 and 200 K for PbSe quantum dots with two different sizes. The field dependent magnetization in range of low field is reproduced in the inset. The vertical lines point out the field at which maximum value of magnetization is observed.

tization is positive at a low field, whereas it is a diamagnetism at a magnetic field higher than 5 kOe. The curves of field dependent magnetization taken at 100 and at 200 K do not change apparently. At a high field of 50 kOe, the negative magnetization is much larger for 6.7 nm PbSe QDs (smaller QDs). The positive magnetization at low fields also seems larger for the smaller QDs (see the inset in Fig. 2). The vertical lines indicate the field where maximum magnetization is observed. If applied field is higher than the indicated field of maximum magnetization, the diamagnetic response will be superior to the paramagnetic response of QDs. Since diamagnetism may break down any possibly magnetic order, we select a field range of lower than the indicated value to carry out the hysteresis loop measurements.

In order to observe the paramagnetic zero-field peak, the differential susceptibility derived from data in Fig. 2 is shown in Fig. 3. The differential susceptibility of PbSe QDs exhibits a positive value near zero field and then decreases to approach a negatively saturated value of susceptibility. The saturated susceptibility is larger than the core diamagnetism of bulk PbSe by several times. The values are about -1.9

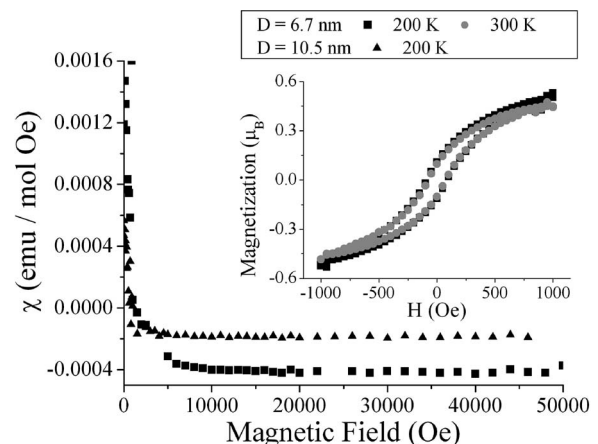


FIG. 3. The differential susceptibility as a functions of field being calculated from the data shown in Fig. 2 (Inset). The hysteresis loops of PbSe quantum dots with a diameter of 6.7 nm.

$\times 10^{-4}$ and -4.0×10^{-4} emu/mol Oe for QDs with sizes of 10.5 and 6.7 nm, respectively. Since a larger field is required to enclose the same amount of magnetic flux for a smaller QD, the fact that a lower field to approach a saturation for the larger PbSe QDs verifies that the magnetic response mainly comes from the QDs. The smaller PbSe QDs give higher paramagnetic zero-field peak and demonstrate a higher value of saturated diamagnetism simultaneously. We conducted measurement of the hysteresis loop from -1 to $+1$ kOe as illustrated in the inset of Fig. 3. The magnetization is estimated in the unit of Bohr magneton per single QD. Unexpectedly, profound hysteresis loops were recorded at both 200 K and room temperature. It therefore suggests that, in the range of low field, ferromagnetic order among the QDs exists even at room temperature.

When the magnetization is estimated on the basis of per PbSe unit cell, its magnitude seems enhanced for smaller QDs. However, we may come to an opposite conclusion in which the magnetization is reduced in the case of 6.7 nm QDs (smaller QDs), as we estimate it on the basis of per single QD. For example, the saturated diamagnetic susceptibilities are -1.9 and -4.0 ($\times 10^{-4}$ emu/mol Oe) for QDs with sizes of 10.5 and 6.7 nm, respectively. The magnitude of the saturated diamagnetism is almost inversely proportional to squares of diameter (D), i.e., D^{-2} . Since the number of PbSe unit cells in a QD is proportional to D^3 , we come to a conclusion of linear dependence on the diameter (D^1), for magnetization of a single QD. This conclusion suggests more electrons orbiting in a larger QD and agrees well with theoretical predictions.

In summary, the magnetic response of PbSe QDs has been studied by measurements of field and temperature dependence of magnetic susceptibility. At low temperatures and fields the paramagnetism dominates the contribution of magnetization, whereas the diamagnetism dominates it at high

temperatures and fields. For smaller PbSe QDs, magnetic susceptibility shifts upward at low fields and shifts to a more negative value at high magnetic fields. The paramagnetic zero-field peak has been observed in the field dependence of differential susceptibility. All of the investigations above imply the existence of spontaneous magnetization in the QD. Surprisingly we have also observed profound hysteresis loops, showing a ferromagnetic order among the QDs even at room temperature.

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