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Different sizes of three-dimensional PbSe quantum dots have been synthesized for the study of orbital magnetic susceptibilities. Two types of orbital susceptibilities have been found, including the Curie susceptibility and finite-size corrections to the Landau susceptibility. The Curie term of a quantum dot manifests itself in the temperature dependence of magnetic susceptibility at low temperatures, while the field dependence of differential susceptibility at high temperatures shows finite-size corrections to the Landau susceptibility. Both of the two kinds of orbital susceptibility, estimated per quantum dot, show linear dependence on the size. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2168444]

Semiconductor and diluted magnetic semiconductor quantum dots (QDs) have drawn a lot of attention since their physical properties can be modified by the quantum confinement effects[1–3] and they possess a potential application in building spintronic devices such as quantum computer.[4] Recently, due to a successful development of synthetic methods, high-quality preparation of many II-VI and IV-VI semiconductor QDs have been carried out and it has become possible to characterize their physical properties, especially the optical properties.[5–9]

Physics at mesoscopic scales often leads to striking phenomena due to intrinsic quantum effects.[10] Magnetic properties of materials, when transferred to the nanophase, may be much different from those in their bulk state. For example, carbon nanotubes, such as two-dimensional structures of graphite, exhibiting large diamagnetic susceptibility and owing mainly to orbital ring currents, have been studied experimentally and theoretically.[11,12] Another example is that below a threshold diameter, Pd and Au nanoparticles, which correspond to para- and diamagnetic metals in bulk states, respectively, may display spontaneous magnetization.[13–15] According to a theoretical calculation, a mesoscopic tube is diamagnetic when the radius is larger than a threshold value, but becomes paramagnetic when its radius is smaller.[10]

Orbital magnetism had been an important theoretical work to understand the magnetic properties of ballistic billiard in mesocopic regime,[16] for example, to explain the magnetization of a large amount of two-dimensional semiconductor QDs which were fabricated by the lithography technique.[20] Two different theoretical approaches were adopted. One was taking quantum dots as atomiclike objects to demonstrate the orientational paramagnetism and precessional diamagnetism which were like the Curie and Langevin susceptibilities of atoms, respectively.[17] The oscillatory paramagnetic susceptibility as a function of the number of electrons in the QD was predicted. The other theoretical method was starting from the Landau susceptibility in bulk states. The free-electron diamagnetic susceptibility was then modified by finite-size corrections.[16,18,19] A zero-field paramagnetic peak which was firstly observed in experiments by Lévy *et al.*[20] was reproduced theoretically. Recently, the experimental report[21] showed information about magnetization of two-dimensional electron system and QDs which were differentiated in their field dependencies. The magnetization of QDs confirmed the zero-field paramagnetic peak.

Although quite a lot of theoretical works have been conducted to simulate the orbital magnetic response of QDs, the experimental studies of both the Curie and finite-size corrections to the Landau susceptibility of QDs have not been reported. With a help of high- quality preparation of monodisperse semiconductor QDs (Refs. 22 and 23) and a careful separation of magnetic contribution from atoms and QDs, we report a direct observation of the two kinds of orbital magnetism.

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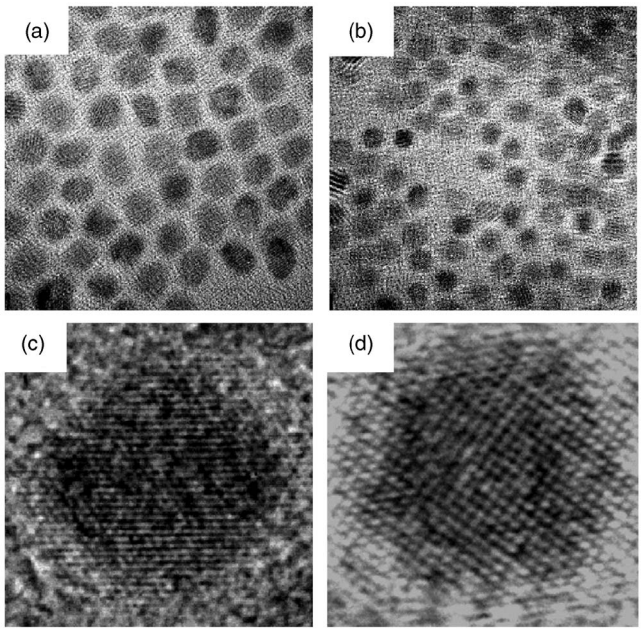

FIG. 1. TEM images of PbSe QDs with diameters of 10.5 nm [(a) and (c)] and 6.7 nm [(b) and (d)]. The image sizes of (a) and (b) are 90×90 nm^2 and the image sizes of (c) and (d) are 12.3×12.3 nm^2 and 7.4×7.4 nm^2, respectively.

7.9 g of selenium powder (99.999%, Aldrich) was added into 100 mL of trioctylphosphine (TOP, 90%, Aldrich). The mixture was stirred for overnight in a glove box to form a clear TOP-Se solution (1*M* for Se). In a typical experiment, 1.081 g of lead acetate trihydrate [$(CH_3CO_2)_2Pb\cdot3H_2O$, 99.99+%, Aldrich, 2.85 mmol], 1.8 mL of oleic acid (90%, Aldrich), and 15 mL of phenyl ether were mixed and heated to 150 °C for 30 min under argon atmosphere. After the solution was cooled to 40 °C, it was transferred to a glove box and mixed with 4.0 mL of TOP-Se stock solution. This room-temperature mixed solution was then rapidly injected into vigorously stirred phenyl ether (15 mL) that was preheated to 150 °C in a three-neck flask equipped with a condenser under argon stream. After the injection, the temperature of the mixture dropped to about 135 °C and then was kept constant at 150–200 °C for 10 min, depending on the desired size of PbSe nanocrystals. The PbSe dispersion was then cooled and ethanol was added to flocculate the nanocrystals which were subsequently separated from solution by centrifugation. The size distribution of PbSe nanocrystals was further narrowed by a size-selection post-treatment using a pair of solvents, hexane/ethanol system.

PbSe QDs with different sizes have been prepared. The size distribution was monitored by using transmission electron microscope (TEM), where the standard deviations are 7.1% and 4.1% for QDs with diameters of 10.5 and 6.7 nm, respectively. The crystalline structure and the spherical shape of the PbSe QDs were confirmed by the high-resolution TEM images shown in Fig. 1. The TEM images were carried out on a JEOL JEM-2010F. Magnetic properties of PbSe QDs were measured, over a temperature range of 2–300 K and a field from 0 to 50 kOe, by a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-7). The magnetization of PbSe QDs is at least ten times larger than the sample holder background which is mainly from the capsule and is about -1×10^{-6} emu at 1 kOe. The susceptibility was calculated by dividing the molar grams of PbSe, not that of QDs.

The as-grown PbSe QDs stabilized with capping agents of both TOP and oleic acid. The total ratio of capping agents in all samples is ~10 wt % which was obtained by using differential scanning calorimetry and thermogravimetric analysis (DSC-TGA). The molecular susceptibilities from TOP and oleic acid are −3.20 and −2.10 $\times10^{-4}$ emu/mol Oe, respectively.[24] The temperature- and field-independent susceptibilities of TOP and oleic acid, which are about −0.06 and -0.06×10^{-4} emu/mol Oe in our samples, are ten times smaller than the diamagnetic susceptibility of PbSe in the bulk state and are neglected. We only subtract the core diamagnetism of PbSe, taken as -1.0×10^{-4} emu/mol Oe,[25] from the raw data. To examine the magnetization from contamination of magnetic impurities, a large-size system of Mn-doped PbSe nanoarrays were synthesized.[23] We have observed that the field dependence of magnetization of PbSe with Mn impurities had paramagnetic response under high magnetic fields while that of the pure PbSe QDs did not have any paramagnetic response at 5 K, even though the temperature dependence of molar susceptibilities and the Curie constants for them both are the same. The following data are solely from the QDs.

How many electrons or holes are there in a QD? If no free electron exists, we cannot observe any orbital susceptibility. A native hole doping of PbSe is typically having a bulk carrier concentration of $\sim10^{18}$ holes/cm^3.[26] It generates less than one hole per QD with a size of 10 nm. Beside doping carriers, it had been established that PbSe, when exposed to the air or oxygen, formed a strong *p*-type surface layer and had high surface charge densities of $2-5\times10^{13}$ carriers/cm^2.[26] We then estimate it being 15–40 holes in the 10-nm-sized QD when exposed to the air.

Temperature-dependent susceptibilities are shown in Fig. 2. The magnetic susceptibilities of the PbSe QDs are given by $\chi=\chi_{C,\mathrm{atom}}+\chi_{L,\mathrm{atom}}+\chi_{C,\mathrm{QD}}+\chi_{L,\mathrm{QD}}+\chi_{\mathrm{Landau}}$, where $\chi_{C,\mathrm{atom}}$, $\chi_{L,\mathrm{atom}}$, $\chi_{C,\mathrm{QD}}$, and $\chi_{L,\mathrm{QD}}$ are the atomic Curie, atomic Langevin, the QD's Curie, and the QD's Langevin susceptibilities, respectively, and χ_{Landau} is the contribution from finite-size corrections to the Landau susceptibility. The filled shells of electrons in PbSe result in a zero susceptibility of the atomic Curie term, and the core Langevin diamagnetism of PbSe is subtracted from the data. The remaining contribution to the temperature-dependent susceptibility is the Curie susceptibility of QDs. It can only be observed at temperatures $T<10$K, and no field dependence of paramagnetism has been observed at a temperature exceeding 5 K. The disappearance of the QD's Curie susceptibility at a slightly higher temperature comes from the degraded quantization since the QDs have a much larger diameter compared with the atomic size. The susceptibility as a function of temperature is then fitted by $\chi=\chi_0+C/(T-T_C)$, where χ_0 is a constant shift, C is the Curie constant, and T_C is the Curie or Weiss temperature. The samples studied under different external fields are listed in Tables I and II. We only subtract the core diamagnetism with a value of -1.0×10^{-4} emu/mol Oe from our raw data.

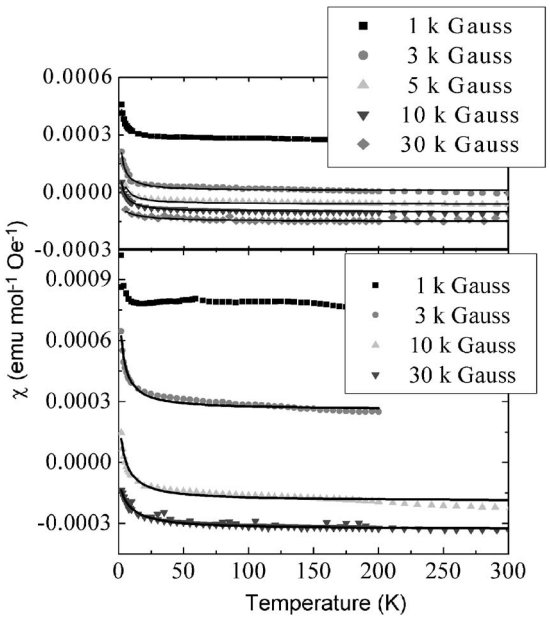

FIG. 2. Temperature dependence of susceptibilities of PbSe QDs under several external fields indicated in the graph. The susceptibilities are estimated per mole of PbSe. The solid lines represent best fitting curves.

The fitted results show the same Curie constants for QDs with the same size and approve good fitting. The Curie constant of 6.7 nm QDs is ~2.8 times of that of 10.5 nm QDs. It roughly corresponds to $(10.5/6.7)^2$, that is proportional to D^{-2}, where D is the size of the QDs. The positive shift of χ_0 is from the orbital Landau susceptibility, not from the Curie susceptibility. The contribution to the negative T_C, the Weiss temperature, is from the orbital Curie susceptibility. An increase of the Weiss temperature with a raising field may indicate a strong interaction in the QD.

A clear evidence of zero-field paramagnetic peak which agrees well with the theory of finite-size corrections to the Landau susceptibility is shown in Fig. 3. The differential susceptibilities of both the 6.7- and 10.5 nm QDs taken at 200 K show paramagnetic with positive value under low fields and a transition to negatively saturated susceptibility under high magnetic fields. The saturated Landau diamagnetism in a high field gives −4.16 and −1.88 $\times 10^{-4}$ emu/mol Oe for 6.7 and 10.5 nm PbSe QDs, respectively. The orbital Landau susceptibility of the QDs per PbSe is several times larger than that of the core diamagnetism of PbSe. The saturated Landau diamagnetism of the QDs varies with the diameter D as a function of D^{-2}. Differential susceptibilities under low magnetic fields are displayed in the inset of Fig. 3 to display its consistency of enhancement in

TABLE I. Fitting results of 10.5 nm PbSe QDs.

H(kOe)	χ_0 (emu/mol Oe)	C (emu K/mol Oe)	T_C (K)
1	2.7×10^{-4}	6.0×10^{-4}	−1.7
3	0.1×10^{-4}	6.9×10^{-4}	−1.5
5	-0.6×10^{-4}	5.6×10^{-4}	−1.4
10	-1.0×10^{-4}	6.1×10^{-4}	−1.9
30	-1.5×10^{-4}	7.4×10^{-4}	−8.6

TABLE II. Fitting results of 6.7 nm PbSe QDs.

H(kOe)	χ_0 (emu/mol Oe)	C (emu K/mol Oe)	T_C (K)
3	2.6×10^{-4}	1.7×10^{-3}	−2.7
10	-1.9×10^{-4}	1.9×10^{-3}	−4.2
30	-3.3×10^{-4}	1.8×10^{-3}	−7.3

the 6.7 nm QDs. The temperature effect on the differential susceptibility is inspected for 6.7 nm QDs. It shows a broader zero-field paramagnetic peak at 5 K. The constant shifts χ_0s, listed in Tables I and II, are plotted in Fig. 3. They tend to lie on the differential susceptibility taken at 5 K.

For a flux quantum threading through a 10 nm QD, a magnetic field up to 520 kOe is needed. The extremely high field is required to see a complete cycle of oscillatory susceptibility. A transition from positive susceptibility to negatively saturated susceptibility in Fig. 3 may be understood by the probing length of the magnetic field. We found that, for the differential susceptibility taken at 200 K, the required fields to approach a negatively saturated susceptibility are ~3 and ~7 kOe for the QDs with sizes of 10.5 and 6.7 nm, respectively. The smaller-size QDs having a higher magnetic field to approach the saturated susceptibility verify that the magnetic response is mainly from the QDs.

We calculate the magnetization of a QD by multiplying the total number of PbSe unit cells and draw the field-dependent magnetization in Fig. 4. It shows a small positive increase in fields lower than 1 kOe and a large decrease in high fields. The high-field magnetization exhibits linear dependence on magnetic fields at higher temperatures. Since the number of PbSe unit cells is proportional to D^3, and the Curie and finite-size corrections to the Landau susceptibilities per mole of PbSe are both proportional to D^{-2}, we find that the orbital magnetic susceptibilities of the QD vary linearly with its diameter as D^1. The results of field-dependent differential susceptibilities and the size dependencies agree well with theoretical calculation of two-dimensional QDs.[19] Here, we use the concept of thermal length $L_T=\hbar v_F/k_BT$ to see the temperature effect. A periodic orbit contributes sig-

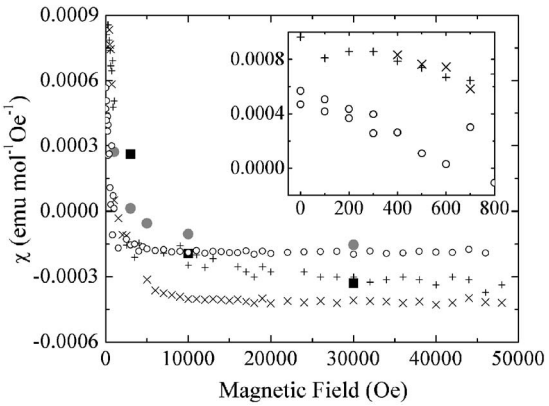

FIG. 3. Differential susceptibilities per mole PbSe. The open circles are calculated from field-dependent magnetization of 10.5 nm QDs at 200 K. The crosses and the pluses represent susceptibilities of 6.7 nm QDs at 200 and 5 K, respectively. The closed circles and squares are χ_0s in Tables I and II of PbSe QDs with diameters of 10.5 and 6.7 nm, respectively. Inset: susceptibility in the low-field regime.

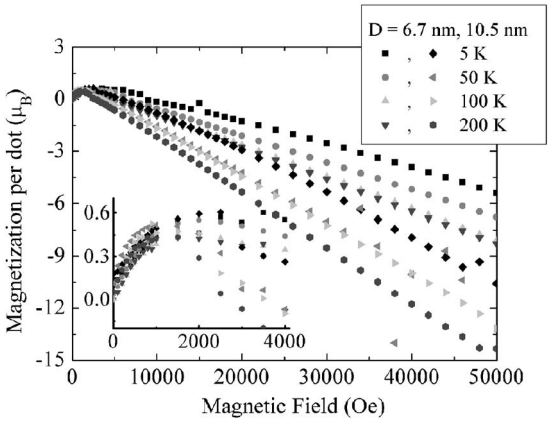

FIG. 4. Field dependence of magnetization per QD under high magnetic fields. Inset: magnetization under low magnetic fields.

nificantly only if the size is of the order or shorter than the thermal length $D<L_T$.[18] This leads to a relation $T<\hbar v_F/k_B D$. As the size of the QDs is smaller, the orbital susceptibility can be observed at a higher temperature. Comparing with previous experiments performed at 0.2 and 8 K for QDs with sizes of 4.5 μm and 550 nm, respectively, the orbital susceptibility of the 10 nm QD can exist up to room temperature.

Two kinds of orbital susceptibilities, including the Curie and finite-size corrections to the Landau susceptibilities, have been observed in the three-dimensional PbSe QDs. The temperature dependence of susceptibility at low temperature shows the Curie susceptibility of the QDs. In addition, the field dependence of differential susceptibility shows zero-field paramagnetic peak and reveals finite-size corrections to the Landau susceptibility. Both the two kinds of orbital susceptibilities display linear dependence on the size of the QD. Since the averaged susceptibility per PbSe unit cell decrease as a function of inverse square of the size, the susceptibilities from the QD disappears in the bulk state. Theories of orbital magnetization of two-dimensional QDs can explain some experimental results of our three-dimensional PbSe QDs.

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