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2007 J. Phys.: Condens. Matter 19 236223

(http://iopscience.iop.org/0953-8984/19/23/236223)

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **19** (2007) 236223 (11pp) doi:10.1088/0953-8984/19/23/236223

A quantum explanation of the abnormal magnetic behaviour in Mn-doped ZnO nanowires

Yousong Gu, Xiaomei Zhang, Xueqiang Wang, Yunhua Huang, Junjie Qi and Yue Zhang[1]

Department of Materials Physics and Chemistry, University of Science and Technology Beijing, Beijing 100083, People's Republic of China

E-mail: Yuezhang@pgschl.ustb.edu.cn

Received 4 December 2006, in final form 29 April 2007
Published 15 May 2007
Online at stacks.iop.org/JPhysCM/19/236223

Abstract

The effective mass approximation is applied to explain the abnormal magnetic behaviour observed recently in Mn-doped ZnO nanowires. The magnetization versus temperature curves have been calculated for nanowires at different radii and carrier densities. Abnormal peaks in the M–T curves are observed at low temperature when the radii of the cylinders are in the nanometre region. Peaks have been observed in the calculated M–T curves for some carrier densities where the Fermi levels are near the peaks of the majority spins in the density of states (DOS) plots, and the peak position moves to the high-temperature region when the radius of the nanowire decreases. The abnormal magnetic peaks in the M–T curve can be explained as a quantum confinement effect of nanowires.

1. Introduction

Recently, diluted magnetic semiconductors (DMSs) have received a lot of attention as new functional semiconducting materials with spin degree of freedom [1]. DMSs with room temperature ferromagnetism have been of great importance in device applications, such as (Zn, Co)O and (Zn, Ni)O [2, 3]. ZnO is a semiconductor with a wide range of applications, such as ultraviolet light emitters, gas sensors, and transparent conductors, etc. Transition-metal-doped ZnO has been investigated as a promising diluted magnetic semiconductor for spintronics. $Zn_{1-x}Mn_xO$ ($x = 0.1$ and 0.3) films prepared by laser molecular beam epitaxy were reported to be ferromagnetic [4]. Recently, we reported an abnormal magnetic behaviour in $Zn_{1-x}Mn_xO$ nanowires: an abnormal peak in the M–T curves located at 55 K under an external magnetic field of 500 Oe [5]. A ferromagnetic hysteresis loop measured at 55 K further ruled out the possibility of an abrupt change of susceptibility due to phase transition, such as residual O_2 condensation [6]. Further investigation has also ruled out other effects, such as substrates [7].

[1] Author to whom any correspondence should be addressed.

Since this abnormal behaviour is observed in nanowires, the quantum size effect may be the origin.

In this paper, we try to explain this abnormal behaviour as a quantum size effect in nanowires in the framework of the effective mass approximation and envelope function scheme.

2. Theoretical model

In order to study the electronic structures of nanowires, the effective mass approximation and envelope function scheme, which is widely applied in semiconductor quantum wells and quantum dots, can be employed [8, 9]. In that scheme, the wavefunction can be written as the product of a slowly varying envelope function and a periodic wavefunction. After the periodic wavefunction has been selected, the physical properties can be determined by the envelope function, and the envelope function can be solved by using effective masses and the effective potential. Nanowires can be modelled as cylinders with carriers confined in it. The carriers can move freely along the z direction, but they are confined within a circle of radius a in the x–y plane. For simplicity, rigid confinement was applied, and the effective potential V can be expressed as:

$$V_{\text{eff}}(\vec{r}) = \begin{cases} 0 & (r \leqslant a) \\ \infty & (r > a) \end{cases} \tag{1}$$

where a is the radius of the cylinder. For nanowires with large radii (e.g. $a > 6$ nm), rigid confinement will not lead to significant deviations from a more realistic effective potential as long as the radii of the nanowires are much larger than the penetration depth into the barrier (less than 1 nm). In a cylindrical coordinate system, the envelope function can be written as:

$$\psi(\vec{r}) = R(r)\Theta(\theta)Z(z) \tag{2}$$

where r, θ and z are the coordinates of a cylindrical coordinate system. The solution to this function can be written as:

$$\psi(r, \theta, z) = J_l(k_r r)\mathrm{e}^{\mathrm{i}l\theta}\,\mathrm{e}^{\mathrm{i}k_z z} \tag{3}$$

where $J_l(k_r r)$ is the lth-order Bessel function of the first kind. Also, the energy of a carrier in a nanowire is:

$$E = E_r + E_z = \frac{\hbar^2 k_r^2}{2m_\parallel} + \frac{\hbar^2 k_z^2}{2m_z}. \tag{4}$$

The boundary condition requires that $\Psi(r, \theta, z) = 0$ when $r = a$, which means that:

$$E_r = \frac{\hbar^2}{2m_\parallel}\left(\frac{\mu_{nl}}{a}\right)^2 \tag{5}$$

where μ_{nl} is the nth root of the Bessel function $J_l(x) = 0$ and $m_\parallel$ is the effective mass in the xy plane. The energy level is discrete, and its value is determined by two quantum numbers n and l: n is the main quantum number and l is the quantum number for angular moment.

Since the length of nanowire is quite long, possible values of k_z can be regarded as continuous. The energy level becomes an energy band, and the density of states per unit length is:

$$n(E_z) = \frac{1}{L}\frac{1}{\Delta E_z} = \frac{1}{2\pi\hbar}\sqrt{\frac{2m_z}{E_z}} \tag{6}$$

where ΔE_z is the energy difference between adjacent states and m_z is the effective mass along the z direction. The total density of states per unit length is the summation of the band with $E_r(n, l) < E$:

$$n_{\text{tot}}(E) = \sum_{nl} n(E - E_r(n, l)). \tag{7}$$

In order to compute the magnetic properties, the magnetic energy should be added to the total energy. For simplicity, only Zeeman-like magnetic energy due to spin is added:

$$E_m = -Bm_s \tag{8}$$

where B is the internal magnetic field, and $m_s = \pm\mu_{\text{B}}$ for up and down spins. The orbital magnetic moment is frozen and does not contribute to the magnetic moment of the nanowires. This kind of treatment is quite usual in solid-state physics. The summation is over all the possible magnetic states:

$$n_{\text{tot}}(E) = \sum_{m} \sum_{nl} n(E - E_r(n, l) - E_m). \tag{9}$$

The occupation numbers of each band follow the Fermi–Dirac distribution,

$$f(E) = \frac{1}{\exp\left(\frac{E-Ef}{kT}\right) + 1}. \tag{10}$$

The total number of electrons is

$$N(T) = \frac{1}{V} \int n_{\text{tot}}(E) f(E)\, \mathrm{d}E \tag{11}$$

and the saturation magnetization is

$$M(T) = \frac{1}{V} \int \sum_{m} \sum_{nl} n(E - E_r(n, l) - E_m) f(E) m_s\, \mathrm{d}E \tag{12}$$

where V is the volume of the nanowire per unit length, $V = \pi a^2$. The E_f value is determined by the density of carriers from equation (11).

3. Results and discussion

3.1. Summary of the experimental results

$Zn_{1-x}Mn_xO$ ($x = 0.05$) nanowires have been prepared on silicon substrates by chemical vapour deposition. Scanning electron microscopy (SEM) observation showed that long and uniform nanowires were formed on Si substrate, as shown in figure 1(a). The diameters of the nanowires is distributed over a range: the estimated mean value is about 50 nm, and the standard deviation is about 20 nm. Detailed high-resolution transmission electron microscopy (HRTEM) observation shows that the nanowires are of single-crystalline wurtzite structure and the growth direction is [0001], as shown in figure 1(b).

The magnetic properties of the obtained nanowires were studied using superconducting quantum interference device (SQUID) equipment (MPMS-5). The M–T curve was measured in an external magnetic field of 500 Oe, as shown in figure 2(a). Large magnetic moments were found at temperatures below 20 K. The saturation magnetic moment ($H = 8000$ Oe) at 5 K is estimated to be 0.77 μ_{B} per Mn atom. An interesting sharp peak was found at 55 K in the M–T curve. The interesting peak contradicts the normal M–T curve, and the new behaviour is considered as an abnormal magnetic behaviour in nanowires. The abnormal behaviour is further confirmed by measurements on samples prepared under the same conditions. A direct magnetic hysteresis curve is measured at 55 K, as shown in figure 2(b). This is an obvious ferromagnetic hysteresis curve, with a saturation magnetic moment ($H = 3000$ Oe) of 0.47 μ_{B} per Mn atom. This indicates that the nanowires is ferromagnetic at 55 K.

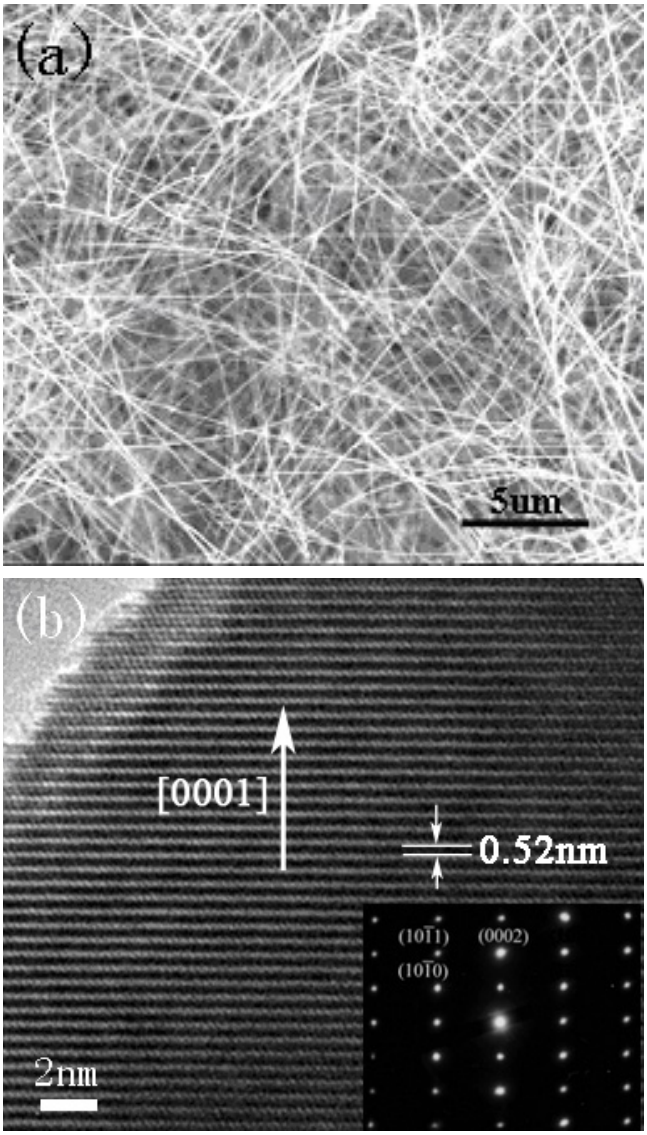

Figure 1. (a) An SEM image of $Zn_{1-x}Mn_xO$ nanowires. (b) HRTEM image of a $Zn_{1-x}Mn_xO$ nanowire; the inset is the corresponding electron diffraction pattern.

In the discussion about this abnormal peak, we notice a similar peak in the M–T curve measured by SQUID [6]. Solid oxygen undergoes an antiferromagnetic to strongly paramagnetic transition at about 43 K, and the susceptibility changes drastically and a peak in the M–T curve was observed. The MPMS system can easily detect the presence of a small amount of condensed oxygen on the sample due to an air leak in the sample chamber. Similar peaks were also found in the M–T curves of $LaCoO_3$, which can be explained by a two-state model in which two electronic states are assumed for the trivalent Co ions: a low-spin nonmagnetic ground state and a high-spin magnetic excited state with an energy difference of 80 meV [10]. This model has been confirmed experimentally by a recent neutron measurement [11].

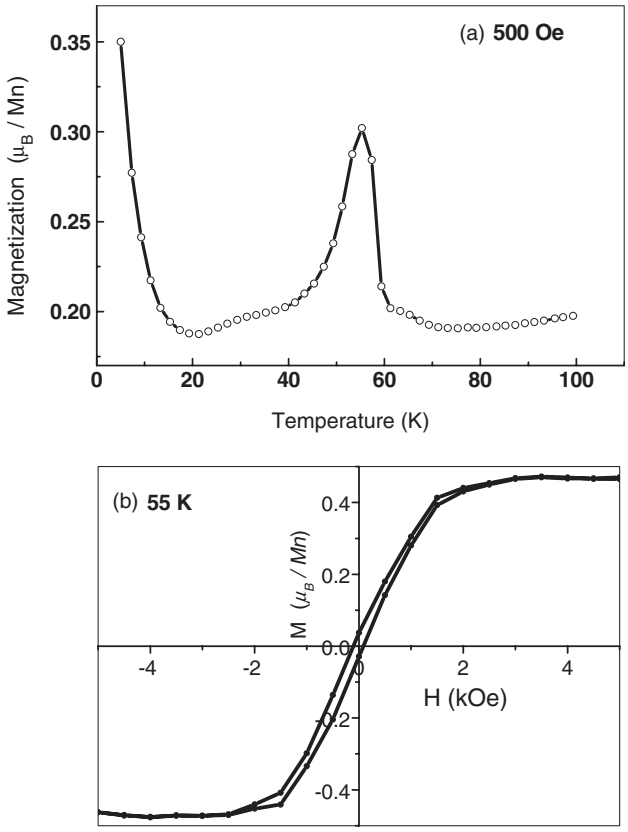

Figure 2. The magnetic properties of $Zn_{1-x}Mn_xO$ ($x = 0.05$) nanowires. (a) The M–T curves in an external field of 500 Oe. (b) Magnetic hysteresis curve measured at 55 K.

The ferromagnetic hysteresis loop measured at 55 K ruled out the above possibility, since the hysteresis loop will be a straight line with a steep slope, which is quite different from a ferromagnetic hysteresis loop. Ferromagnetic ordering existing in our nanowires at 55 K was confirmed.

3.2. Determine the internal magnetic field

The magnetization of Mn-doped ZnO nanowires as a function of temperature can be calculated from equation (12). The effective masses of the carrier are assumed to be $m_{\|} = 0.47\ m_e$ and $m_z = 2.33\ m_e$ [12]. Kim *et al* calculated the ferromagnetic properties of a MnZnO quantum well with these data and found that room-temperature ferromagnetism may be obtained in Mn-doped p-type ZnO [13].

Due to the limitations of our model, we are not able to calculate the magnetic interactions in a self-consistent way with our model. A Zeeman-like magnetic interaction is used with an assumed internal magnetic field. The effect of an internal magnetic field on the calculated magnetic properties is studied. Figure 3 shows the density of states (DOS) per unit length and the magnetization per carrier as a function of temperature for Mn-doped ZnO nanowires with a diameter of 8 nm and a carrier density of $2.5 \times 10^{24}\ m^{-3}$. It can be seen that the energy bands become a doublet due to the spins and the separation increases with the internal magnetic field.

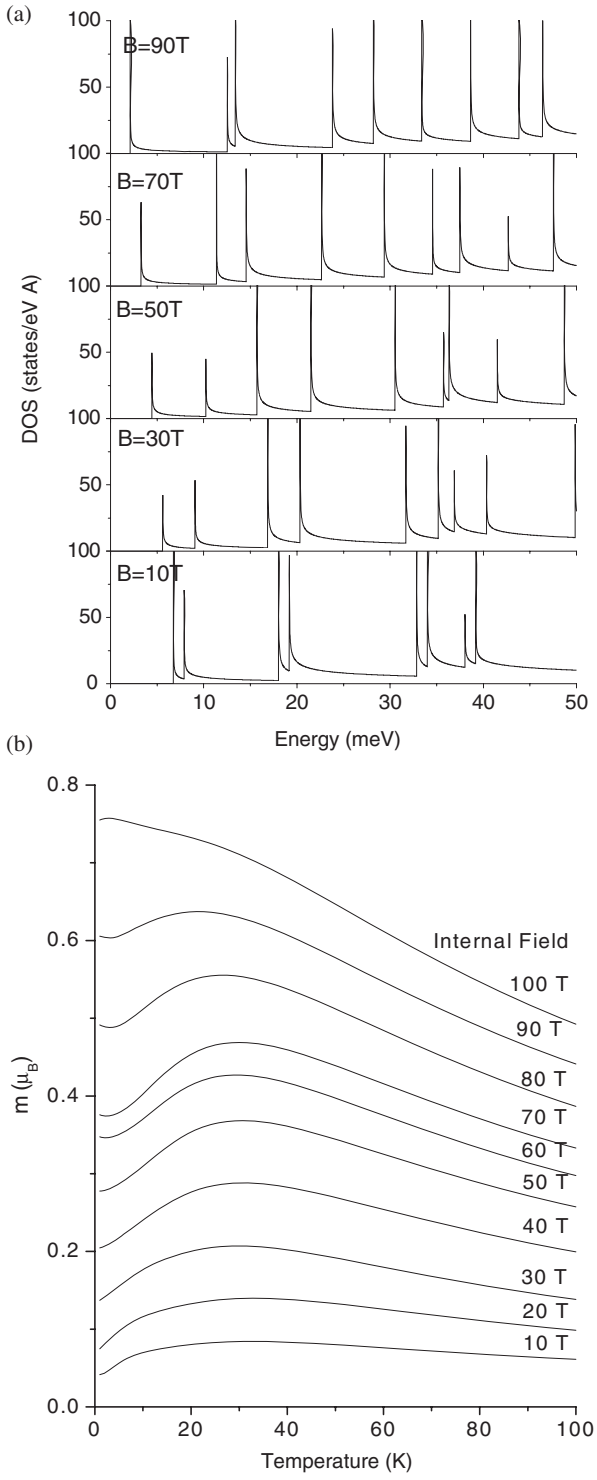

Figure 3. The calculated DOS and M–T curves in different internal magnetic fields for Mn-doped ZnO nanowires with radius $a = 8$ nm.

The separation is so large that there are overlaps in the energy band for an internal magnetic field $B \geqslant 50$ T. By looking at the M–T curves, it can be found that peaks are found at temperatures of about 30 K. When the internal magnetic field is 10 T, the magnetization is low and the peak is just visible. As the magnetic field is increased, the magnetization rises and the peak becomes apparent. However, when the internal magnetic field is increased high above 90 T, the magnetization is too high and the peak disappears. Therefore, we choose a moderate value of 50 T in further calculation. This value is smaller than the typical values in ferromagnetic materials ($B > 100$ T), but it may be acceptable in diluted magnetic semiconductors. The peak value of the magnetization moment per carrier is about 0.4 μ_B, which is reasonable and comparable to experimental values. Further research will be necessary to determine this value in a self-consistent way by taking into account the carrier exchange correlation interactions between the electrons [13].

3.3. Magnetization versus temperature curves and quantum size effect

Magnetization versus temperature curves are calculated for different carrier densities and nanowire radii. Three sets of M–T curves were calculated at $a = 10$, 8 and 7 nm to study the quantum size effects. The selection of the three radii is based on two considerations. First, if the radius of the nanowire was larger than 10 nm, the peak on the calculated M–T curve would be small and move to low temperature region. Second, if the radius was smaller than 6 nm, the deviation from the rigid confinement approximation would be too large.

The calculated density of states (DOS) of nanowires with a radius $a = 10$ nm is shown in figure 4(a). Due to the discrete energy levels $E_r(n, l)$ caused by confinement, there are high peaks in the DOS curve. The average separation between the peaks is about 6 meV (equivalent to 70 K). Due to the internal magnetic field, the energy bands for spin down and spin up are separated. When the Fermi level is near these peaks, the magnetic property is expected to behave in a peculiar way. The calculated M–T curves are shown in figure 4(b). The carrier electron density ranges from 1.0×10^{24} to 6×10^{24} m^{-3}. These are reasonable values for carrier density in Mn-doped ZnO nanowires compared to the calculated DOS of Mn-doped ZnO [14], and the corresponding Fermi energy is 9.0–20.0 meV across three peaks in the DOS plot. The M–T curves are well behaved in the high-temperature region. However, the quantum effect manifested itself in the low-temperature region where the thermal energy is smaller than the peak separation in the DOS plot. As the carrier density increases, the M–T curve changes its shape, corresponding to the change in the Fermi level with respect to the peaks in the DOS. The peak is observed when the Fermi level is close to the majority spin peaks in the DOS plot. The positions of the peaks in the M–T curves are about 20 K for $a = 10$ nm.

In order to study the quantum size effect, the density of states and magnetization versus temperature curves are calculated for nanowires with $a = 8$ nm, and the results are shown in figure 5. The peaks in the DOS are widely separated, with average separations of about 10 meV (corresponding to 120 K thermal energy). The shapes of the M–T curves changed with carrier density (Fermi level). The carrier density ranges from 1.5×10^{24} to 6.0×10^{24} m^{-3}, corresponding to a Fermi level range from 10.0 to 21.0 meV across three peaks in the DOS plot. The peaks in the M–T curves are very apparent compared to the former case. The peak positions in the M–T curves are about 30 K, which is higher than that with $a = 10$ nm.

The calculated DOS plot and M–T curves of nanowires with $a = 7$ nm are shown in figure 6. The peaks in the DOS are very widely separated, with average separations of about 15 meV (corresponding to 170 K thermal energy). The carrier electron density ranges from 1.5×10^{24} to 6.0×10^{24} m^{-3}, corresponding to a Fermi level range from 12.5 to 25.0 meV, across only one peak in the DOS plot due to the large separations between the DOS peaks. The

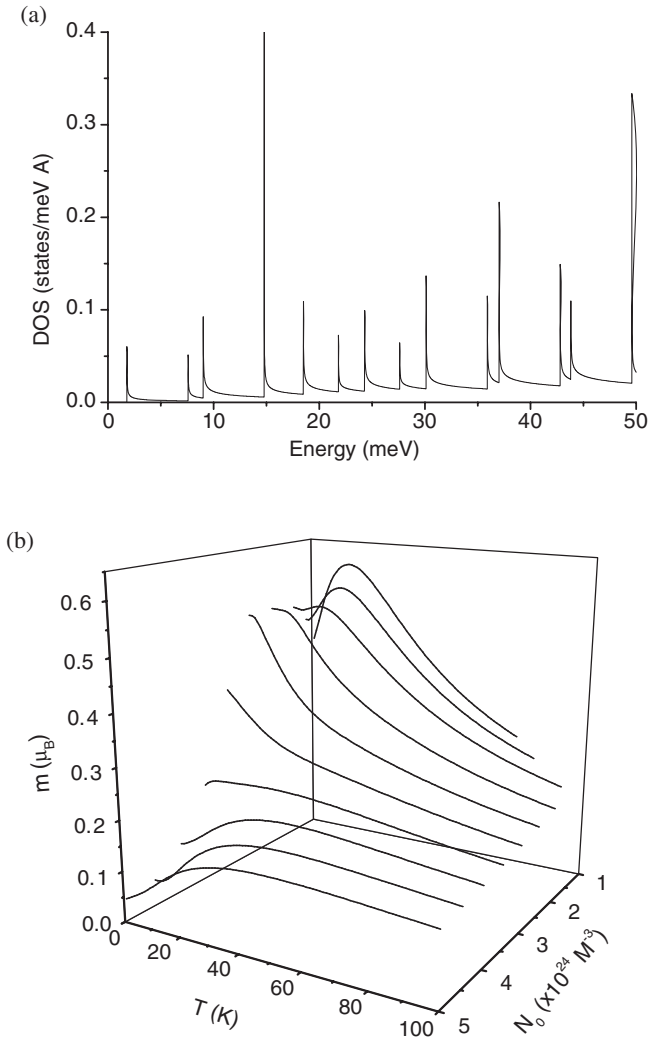

Figure 4. The calculated (a) DOS and (b) M–T curves of Mn-doped ZnO nanowires with radius $a = 10$ nm and internal magnetic field of 50 T.

peaks in the M–T curves are more obvious than the former's. The peaks position in the M–T curves is as high as about 45 K.

From the above calculation, we can see that, due to the quantum size effect, the DOS of carriers in a nanowire has discrete peaks, and the separations between the peaks are determined by the radii of nanowires. Due to these peaks, the calculated M–T curves change shape with carrier density and exhibit peaks at low temperature when the Fermi level is near the peaks of the majority spins. The peak position in the M–T curve increases as the radius of the nanowires decreases.

It can be seen that the experimentally observed abnormal peak in the M–T curve can be explained by the effective mass approximation: peaks are found in the calculated M–T curves. These peaks are caused by the quantum size effect of nanowires. However, the matches are far from perfect: the calculated peak shapes are not sharp enough and the peak positions are lower

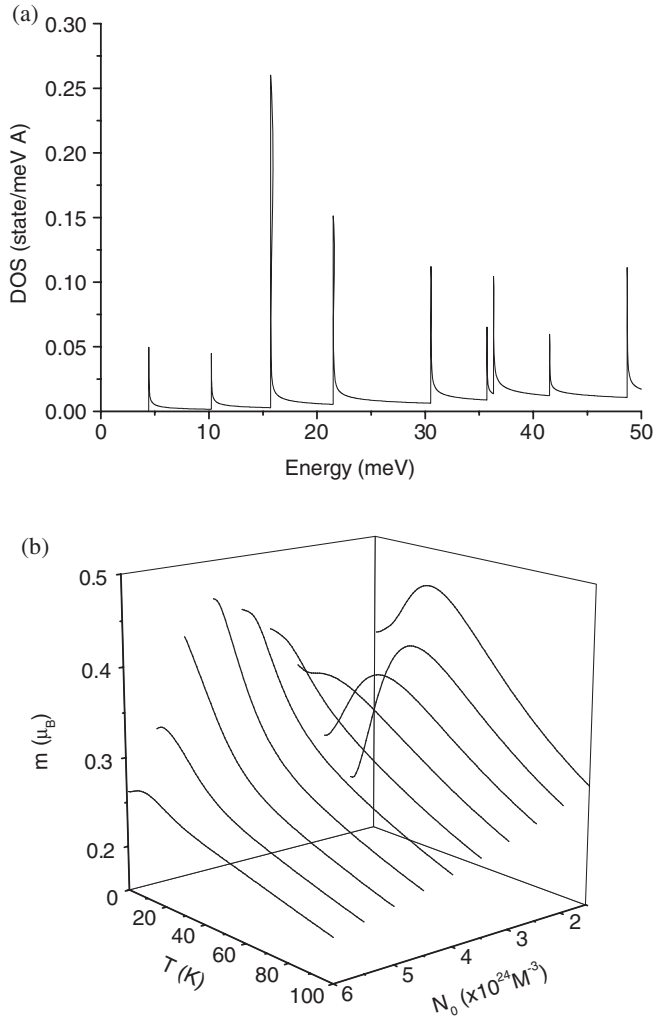

Figure 5. The calculated (a) DOS and (b) M–T curves of Mn-doped ZnO nanowires with a radius $a = 8$ nm and an internal magnetic field of 50 T.

than the experimental data. Experimentally, sharp peaks were found at 55 K in M–T curves for nanowires with diameters of about 50 nm. However, in our calculation, only broad peaks were obtained at temperatures of about 45 K for nanowires with a radius of 7 nm. The shape of the M–T curve changes with the value of the carrier density and peaks are obtained when the Fermi energy is near to the DOS peaks, but this value can be changed by doping and oxygen deficiency and is not well controlled [15, 16].

In our calculation, an infinite barrier and parabolic kinetic energy are assumed for simplicity. Using a realistic effective potential and kinetic energy may lead to more accurate results, but the general trend of the peaks will not be changed for nanowires with $a \geqslant 7$ nm [17]. More rigorous treatment may improve the calculated results, such as taking into account Coulomb interaction, spin fluctuation, finite temperature excitation, exchange correlation etc, and constructing a multi-band Hamiltonian [18]. Further investigations are need.

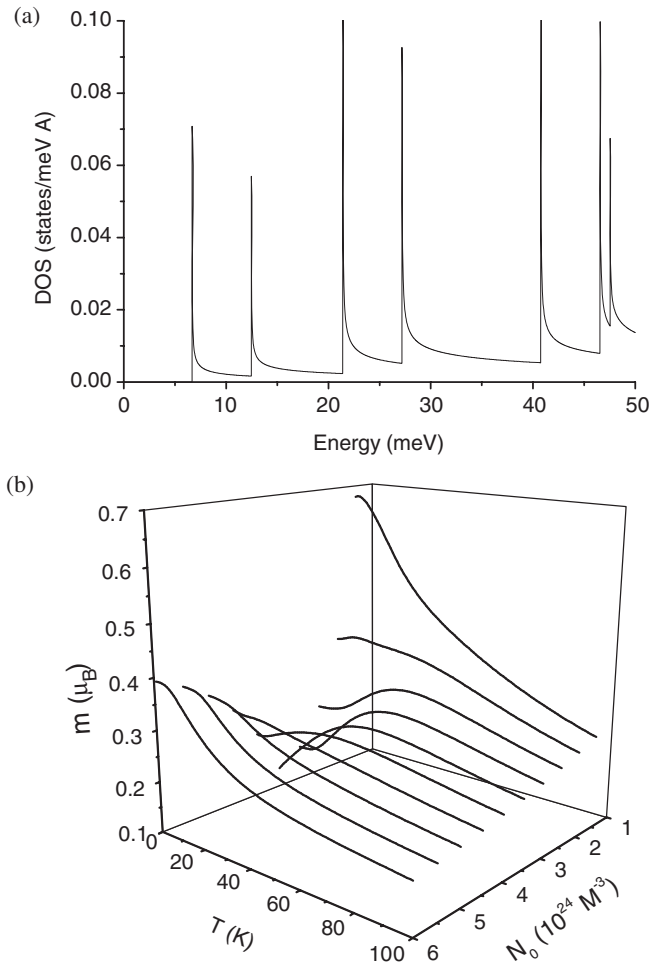

Figure 6. The calculated (a) DOS and (b) M–T curves of Mn-doped ZnO nanowires with a radius of $a = 7$ nm and an internal magnetic field of 50 T.

4. Conclusions

The abnormal magnetic behaviour observed in Mn-doped ZnO nanowires was studied by modelling the carrier in nanowires using the effective mass approximation. Magnetization versus temperature curves at different carrier densities and nanowire radii have been calculated. Peaks have been observed in the calculated M–T curves for certain carrier densities where the Fermi level is near the peaks of the majority spin in the DOS plots, and the peak position moves to the high-temperature region when the radius of the nanowire decreases. The abnormal magnetic peaks in the M–T curve can be explained as a quantum confinement effect of nanowires.

Acknowledgments

This work was supported by the National Science Fund for Distinguished Young Scholars (no. 50325209), the National Natural Science Foundation of China (no. 50572005), and the Key Project of the Chinese Ministry of Education (104022).

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