Internal friction study of phase transformation in self-doping $La_{0.8}MnO_3$ bulk materials



2001 J. Phys.: Condens. Matter 13 3411

(http://iopscience.iop.org/0953-8984/13/14/314)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **13** (2001) 3411–3418 www.iop.org/Journals/cm PII: S0953-8984(01)16695-6

# Internal friction study of phase transformation in self-doping $La_{0.8}MnO_3$ bulk materials

**L Q Zheng and Q F Fang**

Laboratory of Internal Friction and Defects in Solids, Institute of Solid State Physics, Chinese Academy of Sciences, 230031 Hefei, People's Republic of China

Received 9 November 2000, in final form 3 January 2001

**Abstract**

Self-doping $La_{0.8}MnO_3$ bulk material is studied by internal friction, resistance and magnetic susceptibility measurements. Two resistance peaks appear in the curves of resistance versus temperature. In a wide temperature range (80–250 K), quite large magnetoresistance effects are observed under a small field (0.8 T). Two magnetic transitions appear in the ascending temperature measurement. Correspondingly, there are two internal friction peaks in the same temperature range, together with a dramatic change of the elastic modulus. These two internal friction peaks exhibit the characteristics of a phase transition, namely, the peak temperature does not change with frequency, while the peak height increases as the measuring frequency decreases. The correlation between internal friction peaks, resistance peaks and changes in magnetic susceptibility clearly shows the coupling between electron, magnon and phonon. From the position of the internal friction peak at lower temperature and the temperature point where the magnetic susceptibility starts to decrease, we can determine the temperature range for the occurrence of the phase separation process in the self-doping $La_{0.8}MnO_3$ bulk material.

## 1. Introduction

The colossal magnetoresistance materials of the general formula $La_{1-x}A_xMnO_3$, where A is a divalent ion, have recently attracted renewed interest because of their potential in technological applications such as magnetic read–write heads. The use of these materials in such applications is made possible as a result of their interesting magnetic and transport properties. These properties depend crucially on the doping quantity as well as on the nature of the doping element [1]. They are closely related to the mixed valence $Mn^{3+}$ and $Mn^{4+}$. It is also found that the motion of charge carriers establishes the ferromagnetic interaction between $Mn^{3+}$ and $Mn^{4+}$ in the compound with the help of oxygen anions according to the double exchange model [2, 3]. From the viewpoint of changing the $Mn^{3+}$ to $Mn^{4+}$, the most efficient doping method is the so-called self-doping or internal doping [4–7]. However, the properties of the compound might be also influenced by other factors such as chemical inhomogeneity, magnetic inhomogeneity and possible structural inhomogeneity, which are generally related to each

0953-8984/01/143411+08$30.00  

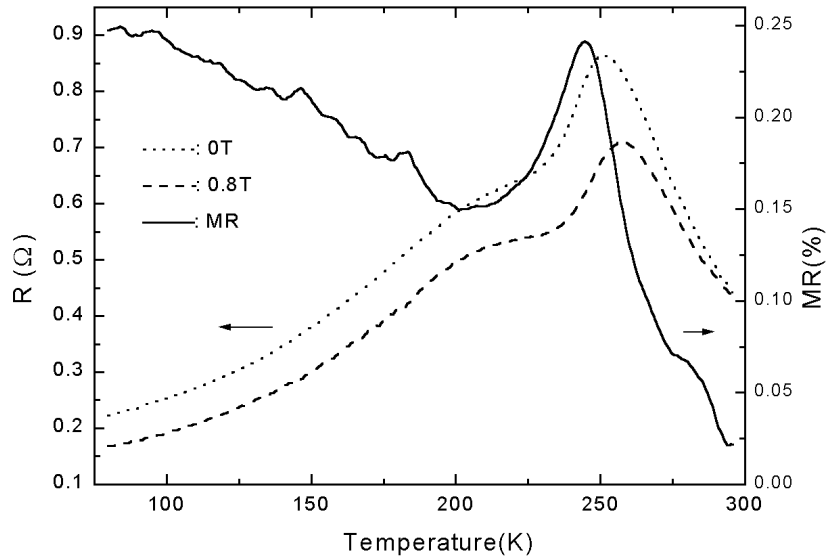


**Figure 1.** Variation of resistance at zero field (dotted line) and at applied field (dashed line), and the corresponding magnetoresistance ratio (solid line) with temperature.

other. This kind of inhomogeneity, or intrinsic phase separation, is a competitive result between the ferromagnetic coupling aroused by double exchange interaction and the anti-ferromagnetic coupling caused by the intrinsic orbital interaction. The phase separation is a process such that the homogenous doped compound is decomposed into two phases at low temperatures: hole-poor anti-ferromagnetic and hole-rich ferromagnetic phases. Most research on phase separation in slightly doped manganites is focused on the theoretical aspects [8–13]. Recently, more and more experimental studies have appeared in the literature [14–20]. These works have opened a new window for the study of physics in the colossal magnetoresistance materials.

The internal friction technique or mechanical spectroscopy, including the measurement of the dynamic elastic modulus, has proved to be a very sensitive tool for studying the phase transition. There are already a few reports on the acoustic velocity (elastic modulus) and acoustic attenuation measurements in the colossal magnetoresistance materials [21–23]. A dramatic change in elastic modulus and a peak in attenuation are observed, which are associated with the ferromagnetic to paramagnetic phase transition. These measurements provided direct evidence of the correlation between electron and phonon. In this paper we present some results obtained in self-doped lanthanum manganites by the low frequency internal friction measurement. Additional to the internal friction peak correlated with the ferromagnetic to paramagnetic phase transition, a new peak at lower temperature is observed in the self-doping specimen, which coincides with a decrease of the magnetic susceptibility and the emergence of an additional resistance peak. This internal friction peak has the characteristics of a phase transition and can be ascribed to the phase separation in self-doping manganites.

## 2. Experiment

Polycrystalline samples of $La_{0.8}MnO_3$ were prepared through a conventional solid state reaction with the starting materials of $La_2O_3$ and $MnCO_3$ powders. Stoichiometric amounts of these powders were mixed and heated at 1273 K for 24 hours in alumina crucibles. After regrinding, the black powders were sintered at 1373 K. Finally, these powders were pressed

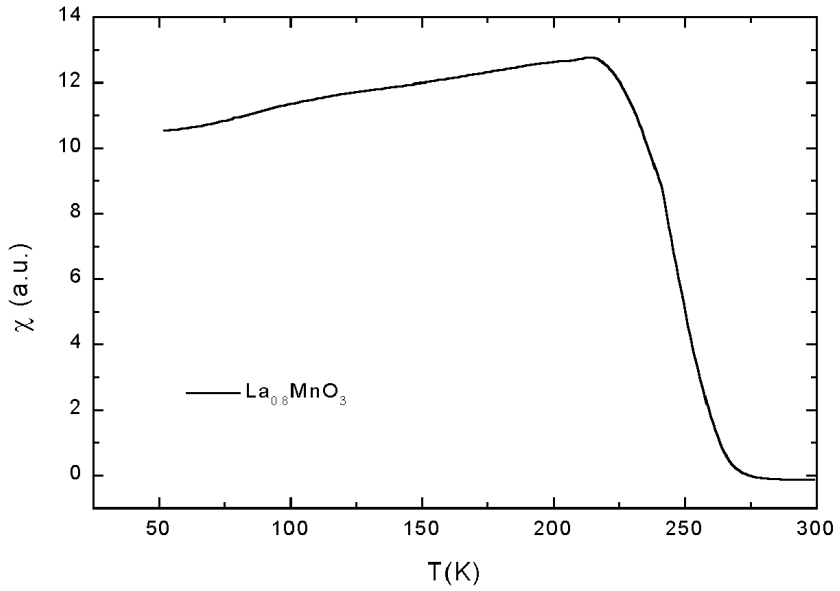


**Figure 2.** Temperature dependence of the ac magnetic susceptibility $\chi$ measured at a frequency of 1000 Hz and a magnetic field of 0.15 mT.

into a mould and sintered for 24 hours at 1523 K. Low-field ac susceptibility between 50 K and 300 K was measured by using a mutual inductance bridge at a frequency of 1000 Hz and a field of 0.15 mT. The resistance of the bulk material was measured in the temperature range of 70–300 K under zero field and a 0.8 T magnetic field by the four-probe technique. The magnetoresistance ratio, MR, was calculated by $\mathrm{MR} = 1 - R(H)/R(0)$, where $R(H)$ and $R(0)$ are the resistance in applied and zero field respectively. The dimension of the specimen for internal friction measurement is about $76 \times 1.5 \times 3$ mm$^3$, and the measurement frequency ranges from 0.1 Hz to 2.0 Hz.

## 3. Results and discussion

Figure 1 shows the temperature dependence of the electric resistance for a $La_{0.8}MnO_3$ sample in the temperature range of 70 K to 300 K. It is clear that two resistance peaks appear. The first $R$ peak at about 250 K corresponds to the metal–semiconductor (M–S) transition. The second small peak is situated at about 200 K after subtraction of the background, indicating that there exists a non-metallic phase in the sample at low temperature. We found that this small $R$ peak results from the non-metallic phase, an anti-ferromagnetic $La_xMnO_3$ phase, as evidenced in the remaining parts of this paper. When a magnetic field of 0.8 T is applied, the first $R$ peak shifts toward higher temperature and the whole $R$–$T$ curve becomes lower. A maximum of MR effect as large as 25% appears just below the M–S transition. At lower temperature the MR effect increases with decreasing temperature and maintains a relatively high value at low temperature, which can be partially ascribed to the scattering effect of electron spin on grain boundaries or domain walls.

From the curve of magnetic susceptibility $\chi$ versus temperature, as shown in figure 2, two steps of magnetization can be seen. The first one is a dramatic increase of $\chi$ with decreasing temperature, indicating a paramagnetic to ferromagnetic phase transition, which

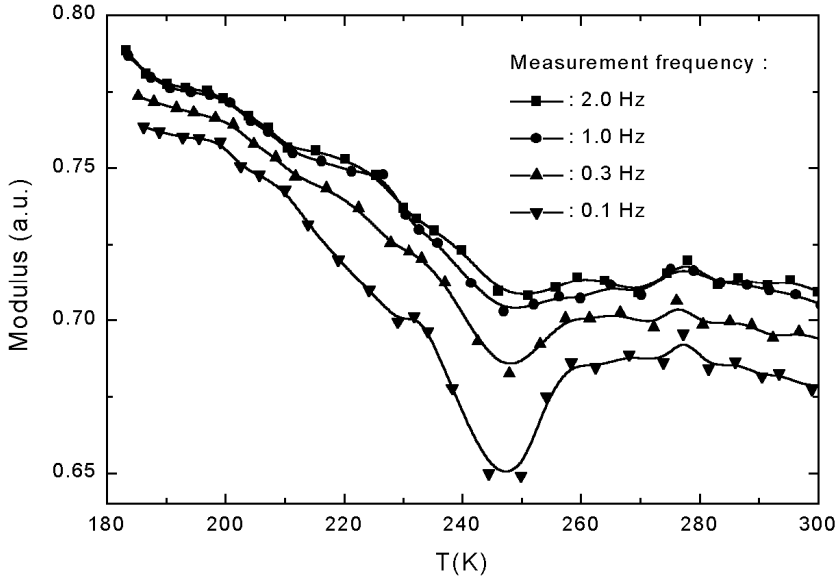


**Figure 3.** The variation of the dynamic elastic modulus with temperatures for a $La_{0.8}MnO_3$ sample obtained by the force vibration method in the frequency range 0.1–2.0 Hz.

coincides very well with the M–S transition at about 250 K and can be understood according to the double-exchange theory. The second one is a continuous decrease of $\chi$ with decreasing temperature starting at about 218 K, implying the existence of an anti-ferromagnetic phase in the sample. In other words, after the paramagnetic to ferromagnetic transition, a ferromagnetic to anti-ferromagnetic transition has occurred, or the ferromagnetic phase has separated into two phases (phase separation): a new anti-ferromagnetic phase is distributed in the matrix phase. Concerning how the second magnetization is related to the small *R* peak and at what temperature the phase separation occurred, the internal friction measurement could give us decisive evidence.

The dynamic elastic moduli at four different frequencies as functions of the temperature are shown in figure 3. The internal frictions of the $La_{08}MnO_3$ sample measured by the force vibration method with ascending temperature are displayed in figure 4. As shown in the figures, the elastic modulus remains almost constant on the high temperature side, but starts to decrease when the temperature is lower than 260 K. After passing through a minimum at about 248 K, the elastic moduli begin to increase with decreasing temperature. The internal friction begins to increase from the background at about 260 K, and develops a clear peak around 247 K where the modulus has a local minimum. With further decrease of temperature, another internal friction peak appears around 225 K. Although these two peaks overlap with each other, they can be well resolved within the range of experimental errors. In the temperature range around the lower temperature peak it is difficult to detect any abrupt change of the modulus in the increasing background, which is consistent with the x-ray analysis result [24] that in this temperature range the lattice parameters change smoothly with temperature.

With decreasing frequency, these two internal friction peaks increase in height but hardly change their positions, as shown in figure 4, where the two peaks are situated at 247 K and 225 K respectively. The inverse proportionality of the peak height with the measurement frequency and the invariance of the peak position by changing frequencies are typical features

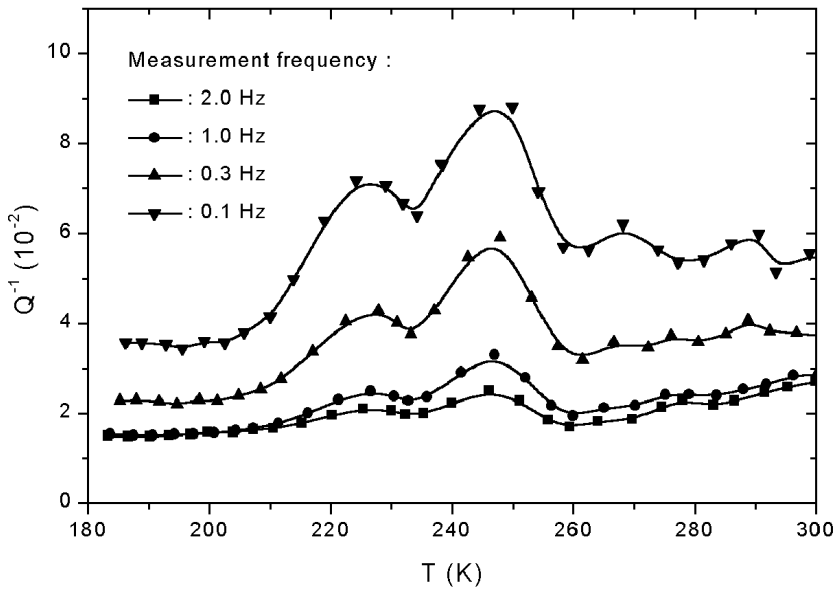


**Figure 4.** The variation of the internal friction with temperature obtained by forced vibration. The measurement frequencies are 0.1, 0.3, 1.0 and 2.0 Hz respectively. The two internal friction peaks increase in height but do not shift in position when frequency decreases.

for phase transition. The corresponding dynamic elastic modulus with a local minimum at 248 K also characterizes the nature of phase transitions, so these two peaks are originated from phase transitions. The small modulus change corresponding to the second internal friction peak (figure 3) implies that the phase transition corresponding to this peak occurred incompletely, or in other words, only a small part of the matrix phase is transited into the new phase. This conclusion is in agreement with the facts that the magnetic susceptibility saturates at a relatively high value at low temperature and the resistance has a relatively large background in the temperature range of the second resistance peak.

In consideration of the different magnetic ordering temperatures of the specimen, the inhomogeneous local lanthanum vacancies and lattice distortion may lead to the two-step magnetization, because the nature of the doping element modifies the electron–phonon coupling as well as the magnetic interaction [25]. The coexistence of the ferromagnetic and anti-ferromagnetic phases has been reported previously and is explained by the intrinsic phase separation of the holes into micro-domains of the ferromagnetic phase [14, 15]. If the carrier density is not enough to make the entire crystal ferromagnetic, unsaturated magnetization is aroused. The transition from the ferromagnetic metal at finite hole density to the anti-ferromagnetic insulator state of the hole-free limit occurs, and the microscopically charged inhomogeneous state is then stabilized. This phenomenon is similar to a phase diagram observed by Yunoki and coworkers [26, 27]. From their numerical calculations, particularly surprising was an observation of the presence of the phase separation between hole-poor anti-ferromagnetic and hole-rich ferromagnetic regions.

Therefore, the first internal friction peak around 247 K, which coincides with the first *R* peak and the dramatic increase of magnetic susceptibility, is associated with the paramagnetic to ferromagnetic transition or M–S transition. The internal friction peak at 225 K, where the magnetic susceptibility starts to decrease, corresponds to a phase separation in the sample.

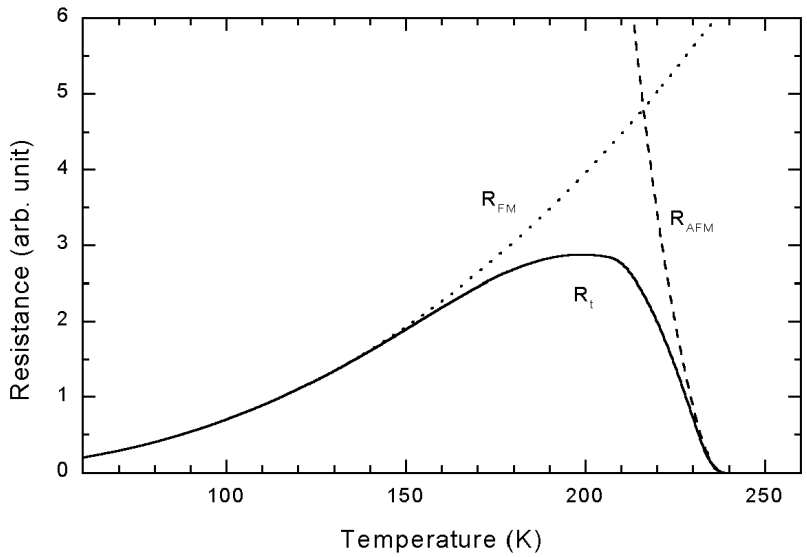


**Figure 5.** Schematic illustration of the appearance of the small resistance peak at about 200 K. Here $R_{FM}$ and $R_{AFM}$ denote the resistance of the ferromagnetic metallic phase and the anti-ferromagnetic non-metallic phase respectively. $R_t$ is the resultant resistance contributed by $R_{FM}$ and $R_{AFM}$ in parallel connection, $R_t = R_{FM}R_{AFM}/(R_{FM} + R_{AFM})$.

This phase separation is a process such that the anti-ferromagnetic phase deposits from the ferromagnetic matrix phase. The existence of an apparent internal friction peak associated with phase separation implies that the process of phase separation occurs in a narrow temperature range around 225 K, the peak temperature of the internal friction peak. Usually we can take the peak width as the temperature range in which the phase separation occurs. In the present case, the phase separation may occur in the range from 235 to 210 K as estimated from the width of the second internal friction peak in figure 4.

It is necessary to point out that the position of the first internal friction peak does not coincide exactly with the first $R$ peak and the dramatic increase of $\chi$, but with a difference of 1–3 K. This may come from the different sample for internal friction measurement and for electric and magnetic measurement. However, the lack of coincidence of the small $R$ peak with the second internal friction peak, which has a difference of 25 K in position, cannot be ascribed to this reason, and may be probably understood as follows. After the paramagnetic to ferromagnetic transition, the ferromagnetic metallic state (FM) is built up in the sample. At lower temperatures, this FM phase alone is unstable against a phase mixture state, and therefore a hole-poor or hole-free anti-ferromagnetic non-metallic phase (AFM) is deposited from the matrix FM phase (phase separation). This process of phase separation can be reflected by the second internal friction peak and the critical temperature point where the magnetic susceptibility starts to decrease. However, the resistance does not exhibit a peak at the temperature where the phase separation occurred, because the resistance of the AFM phase ($R_{AFM}$) is still small due to the small phase amount or small intrinsic resistivity at that temperature. Considering the configuration of FM and AFM phases, the total resistance can be equivalent to a resistance $R_0$ contributed by the main FM matrix phase plus a resistance $R_t$, $R_t = R_{FM}R_{AFM}/(R_{FM} + R_{AFM})$, which comes from $R_{AFM}$ and the resistance of some FM phase ($R_{FM}$) in parallel connection. The $R_0$ gives rise to the supposed background in figure 1. With further decrease of the temperature, the $R_{FM}$ will decrease further, and the

$R_{AFM}$ will increase exponentially due to its non-metallic feature. So at a suitable temperature, the resistance resulting from the parallel connection of $R_{AFM}$ and $R_{FM}$ will reach a peak value. Hence, it is not surprising that the small resistance peak is not coincident with the second internal friction peak, but they are both originated from the phase separation process.

Figure 5 schematically illustrates the appearance of this resistance peak around 200 K. In figure 5, we adopted $R_{FM} = R_1 + aT^{2.5}$ [28] with $R_1 = 6 \times 10^{-5}$ and $a = 7 \times 10^{-6}$ K$^{-2.5}$, and $R_{AFM} = g(T)R_2 \exp(E/kT)$ with $R_2 = 0.01$ and $E = 0.12$ eV [29], where $g(T)$ is a steplike function of temperature reflecting variations of the relative volume fraction of AFM phase. According to the variation of internal friction and resistance with temperature, the temperature of 235 K, at which the second peaks of internal friction and resistance begin to appear, can be defined as the start-temperature of the phase separation. The temperature of 210 K where the second internal friction peak disappears can be taken as the end-temperature of the process of phase separation. Therefore the function $g(T)$ could be defined as $g(T) = 1$ for $T \leqslant 210$ K and $g(T) = 0$ for $T \geqslant 235$ K, and in the interval of 210 K $< T <$ 235 K $g(T)$ is supposed to decrease linearly from 1 to 0 with increasing temperature. Here the values of parameters $R_1$, $a$ and $R_2$, which are dependent on the amounts and the intrinsic resistivity of AFM and FM phases, are so chosen that the peak of the resultant resistance $R_t$ locates at about 200 K. Because we do not know the intrinsic resistivity of AFM and FM phases, it is impossible to deduce the exact amount of AFM phase from figure 5. However, if we have some information about the chemical composition and the intrinsic resistivity of AFM and FM phases, it would be possible to estimate the evolution of the exact volume fraction of AFM phase on the basis of this model.

## 4. Conclusions

In conclusion, two subsequent steps of magnetization occur in the self-doping $La_{0.8}MnO_3$ bulk materials, which lead to two $R$ peaks observed in the $R$–$T$ curve. The complex magnetic and transport behaviours in the specimens could originate from the so-called phase separation (PS). Correspondingly, two internal friction peaks are observed. The first one is associated with the paramagnetic–ferromagnetic transition and/or the M–S transition, indicating clearly the coupling between the electron, magnon and phonon. The second internal friction peak at lower temperature originates directly from the phase separation process, which occurred in the temperature range where the internal friction peak appears. This low-temperature internal friction peak, together with the low-temperature resistance peak and the decrease in magnetic susceptibility, provides direct experimental evidence of the phase separation in self-doped lanthanum manganites. The magnetic heterogeneity may also play an important role in determining the magnetoresistance effect.

## References

[1] Hwang H Y, Cheong S-W, Radaelli P G, Marezio M and Batlogg B 1995 *Phys. Rev. Lett.* **75** 914
[2] Zener C 1951 *Phys. Rev.* **82** 403
[3] Anderson P W and Haswgaua H 1955 *Phys. Rev.* **100** 675
[4] de Silva P S I P N, Richards F M, Cohen L F, Alonso J A, Martinez-Lope M J, Casais M T, Thomas K A and MacManus-Driscoll J L 1998 *J. Appl. Phys.* **83** 394
[5] Gupta A, McGuire T R, Duncombe P R, Rupp M, Sun J Z, Gallagher W J and Xiao G 1995 *Appl. Phys. Lett.* **67** 3494
[6] Manoharan P S, Kumar D and Hegde M S 1995 *J. Solid State Chem.* **117** 420
[7] Pignard S, Vincent H and Senateur J P 1997 *J. Appl. Phys.* **82** 4445
Pignard S, Vincent H and Senateur J P 1998 *Appl. Phys. Lett.* **73** 999

[8] Zou Liang-Jian, Zheng Q-Q and Lin H Q 1997 *Phys. Rev.* B **56** 13 669
[9] Nagaev E L 1998 *Phys. Rev.* B **58** 816
Nagaev E L 1998 *Phys. Rev.* B **58** 2415
[10] Arovas D P and Guinea F 1998 *Phys. Rev.* B **58** 9150
[11] Yi H and Yu J 1998 *Phys. Rev.* B **58** 11 123
[12] Golosov D I, Norman M R and Levin K 1998 *Phys. Rev.* B **58** 8617
[13] Moreo A, Mayr M, Feiguin A, Yunoki S and Dagotto E 2000 *Phys. Rev. Lett.* **84** 5568
[14] Allodi G, De Renzi R, Guidi G, Licci F and Pieper M W 1997 *Phys. Rev.* B **56** 6036
[15] Moreo A, Yunoki S and Dagotto E 1999 *Science* **283** 2034
[16] Uehara M, Mori S, Chen C H and Choeng S-W 1999 *Nature* **399** 560
[17] Kumagai K, Iwai A, Tomioka Y, Kuwahara H, Tokura Y and Yakubovskii A 1999 *Phys. Rev.* B **59** 97
[18] Fäth M, Freisam S, Menovski A A, Tomioka Y, Aarts J and Mydosh J A 1999 *Science* **285** 1540
[19] Raquet B, Anane A, Wirth S, Xiong P and Von Molnar S 2000 *Phys. Rev. Lett.* **84** 4485
[20] Frontera C, Garcia-Munoz J L, Llobet A, Respaud M, Broto J M, Lord J S and Planes A 2000 *Phys. Rev.* B **62** 3381
[21] Li X-G, Chen H, Zhu C F, Zhou H D, Zheng R K and Zhang J H 2000 *Appl. Phys. Lett.* **76** 1173
[22] Zhu Changfei and Zheng Renkui 1999 *Phys. Rev.* B **59** 11 669
Zhu Changfei and Zheng Renkui 1999 *Appl. Phys. Lett.* **74** 3504
[23] Li Kebin, Li Xijun, Liu Changsong, Zhu Zhengang and Du Jiaju 1997 *Phys. Rev.* B **56** 13 662
[24] Zheng L Q and Fang Q F *Phys. Status Solidi* a **184**
[25] de Brion S, Ciorcas F and Chouteau G 1999 *Phys. Rev.* B **59** 1304
[26] Yunoki S, Moreo A, Hu J, Capponi S, Poibanc D and Furukawa N 1998 *Phys. Rev.* B **58** 6414
[27] Yunoki S, Hu J, Malrezzi A, Moreo A, Furukawa N and Dagotto E 1998 *Phys. Rev. Lett.* **80** 845
[28] Schiffer P, Ramirez A P, Bao W and Choeng S-W 1995 *Phys. Rev. Lett.* **75** 3336
[29] Pichett W E and Singh D J 1996 *Phys. Rev.* B **53** 1146