The influence of tilt angle on the CMR in $Sm_{0.6}Sr_{0.4}MnO_3$

I.A. Abdel-Latif [a],[*], A. Hassen [b], C. Zybill [c], M. Abdel-Hafiez [b],
S. Allam [d], Th. El-Sherbini [d]

[a] Reactor Physics Department, NRC, Atomic Energy Authority, Abou Zabaal P.O. 13759, Cairo, Egypt
[b] Physics Department, Faculty of Science, Fayoum University, Al-Fayoum, Egypt
[c] Physics Department, GUC, Cairo, Egypt
[d] Laboratory of Laser and New Materials, Faculty of Science, Cairo University, Giza, Egypt

Abstract

In the present work, the structural and transport properties of $Sm_{0.6}Sr_{0.4}MnO_3$ polycrystalline sample were investigated. The sample was prepared using solid-state reaction technique. X-ray diffraction (XRD) showed a single-phase sample. The dc resistivity and magnetoresistance (MR) were measured, in the temperature range from 40 K up to 300 K, using a cryogenic system capable of applying a magnetic field up to 5 T. A transition at $T_p \sim 89$ K was observed. This transition is shifted towards higher temperatures under the effect of applied magnetic field. At low temperature, $T \sim 70$ K, positive colossal magnetoresistance CMR values of 97% at magnetic field 2 T was observed and reached 99.7% at 5 T.
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1. Introduction

During the last few decades the world scientific attention was concentrated on studying the unusual magnetic and electric properties of rare earth manganites doped with divalent elements. These compounds could be used as a magnetic storage media. The general chemical formula is $R_y A_{1-y} MnO_3$, where R is a rare earth element, A is a divalent element like Ca, Sr, Ba,. . .. These compounds are known to crystallize with the orthorhombic distortion of the perovskite-like structure [1]. The R sites are surrounded by quite distorted 12 oxygen atoms polyhedra while the oxygen octahedron around the Mn atoms is less distorted. When an octahedron is tilted in some particular way, it causes tilting of the neighboring octahedra. The simple formula of both the [b] tilt and [c] tilt are given in Ref. [2]. The first-order approximation of [b] and [c] tilts are defined in Ref. [2] according to the following formula: [b] tilt $\sim (180 - \alpha)/2$ and [c] tilt $\sim (180 - \beta)/2$ where α and β are Mn–O1–Mn and Mn–O2–Mn angles, respectively. These angles are the basic

parameters in the magnetic and the electronic behavior in such a compound because they govern the interaction between the two Mn ions.

In 1950 the striking correlation between the magnetic ordering and conductivity was discovered [3,4] and it was the beginning of further research to understand such correlation. After that the concept of double exchange was suggested by Zener [5]. When some of the R^{3+} are replaced by A^{2+} part of the Mn element will become tetravalent such that this Mn^{4+} is equivalent to the value of A^{2+}. Electronic exchange between Mn^{4+} and Mn^{3+} ions is occurred via oxygen ions and these electrons have the same spin so that the compound becomes ferromagnetic (FM) and conducting. The transport of charge between Mn^{4+} and Mn^{3+} can occur only via simultaneous hopping of e_g-electrons from Mn^{3+} to the O^{2-} and from the O^{2-} to t_{2g} electrons as a result of high spin of the d-electrons [6]. The doping produces an increase in the Mn^{3+}/Mn^{4+} ratio that makes it easier for electrons to hop between the Mn ions thus creating tendency for ferromagnetic interactions rather than the antiferromagnetic (AFM). The AFM interaction dominates if the electrons are more localized so that the strong magnetic field makes the localized spins aligned, which enhances e_g electrons hopping and reduces resistivity [7]. The magnetoresistive behavior is one of the inter-

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* Corresponding author. Tel.: +20 10 7047854.
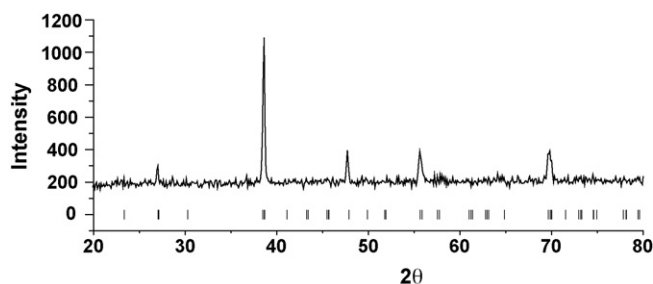E-mail address: ihab_abdellatif@yahoo.co.uk (I.A. Abdel-Latif).

Fig. 1. XRD pattern of $Sm_{0.6}Sr_{0.4}MnO_3$.

Fig. 2. Temperature variation of resistivity at 0 T magnetic field of $Sm_{0.6}Sr_{0.4}MnO_3$ polycrystalline sample (in heating as well as in cooling).

esting properties of these compounds. The correlation between the structure of such compounds and their electrical and magnetic properties plays an important role in understanding these unusual properties [8]. $Sm_{1-x}Sr_xMnO_3$ is one of the manganites which exhibits the colossal magnetoresistive property. Many researches are devoted to study this interesting topic and scientists are willing to improve the characteristic of such compounds [9–16].

In the present paper, study of the CMR and its relation with the crystal structure of $Sm_{0.6}Sr_{0.4}MnO_3$ is presented.

2. Experimental details

$Sm_{0.6}Sr_{0.4}MnO_3$ sample was prepared using solid-state reaction method from initial pure oxides; Sm_2O_3, Mn_2O_3 and carbonate $SrCO_3$. These compounds were mixed together within the appropriate ratios then milled and pressed in disc form. The obtained disc was fired at 950 °C for 12 h in air. The sample was fired again at 1350 °C for 72 h, after repletion of milling and pressing process. Disc of 12 mm diameter was obtained. The XRD measurements were performed using a Diano diffractometer with Co Kα radiation. The XRD test showed that the $Sm_{0.6}Sr_{0.4}MnO_3$ sample exhibits a single-phase with orthorhombic structure. The resistivity–temperature dependence $\rho(T)$ was measured using standard four-probe technique (a cryogenic system capable of applying a magnetic field up to 5 T) in the temperature range from 50 K to 300 K. Both cooling and heating runs were considered.

3. Results and discussions

The XRD pattern is illustrated in Fig. 1. X-ray diffraction analysis was carried out using the program MRIA [17]. The results of XRD analysis that is based on Reitveld method showed that $Sm_{0.6}Sr_{0.4}MnO_3$ has an orthorhombic crystal structure of space group P_{nma}. The quality factors of the agreement between the observed and the calculated profiles are $\chi^2 = 1.251$, $R_p = 5.93$ and $R_w = 7.63$. The Sm/Sr atoms have (x, 1/4, z) coordinates while the Mn atoms have (0, 0, 1/2) coordinates. Concerning the oxygen atoms; four of them occupy the (x, 1/4, z) coordinates and eight have (x, y, z) coordinates. The x and z of Sm/Sr atoms have the values; 0.0170 and 0.0214 while their values for O (1) atoms are 0.5290 and 0.0310, respectively. The O (2)
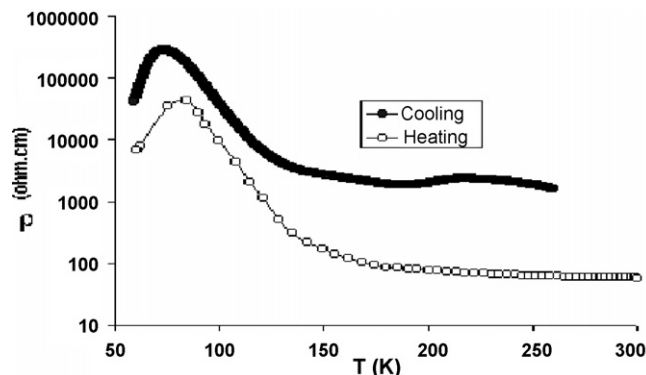
atoms coordinates x, y and z are −0.2678, −0.0026, 0.2398, respectively. The lattice parameters and Mn–O bond lengths of $Sm_{0.6}Sr_{0.4}MnO_3$, prepared in this paper compared with similar one in Ref. [10] are given in Table 1.

It is clear that, there is a good agreement between the lattice constants in both samples however, a difference was found only in the bond length of Mn–O. This deviation in the result of the bond length can be attributed to the different values of the octahedral tilting (MnO_6). The tilt of MnO_6 is calculated according to the well-known formula given in Ref. [2]. The tilt angles of the sample under-investigation are [b] tilt ∼ 6.8755° and [c] tilt ∼ 1.05725° and they have small values compared with those calculated for the sample of Ref. [10] namely; [b] tilt ∼ 10.65° [c] tilt ∼ 10°. This is an indication that in our sample there is less distortion on the MO_6 octahedron than that in the sample of Ref. [10].

There is a difference in the resistivity measurements with increasing and decreasing temperature. The variation in resistivity–temperature dependence behavior of $Sm_{0.6}Sr_{0.4}MnO_3$ at zero magnetic field in the case of heating from the cooling process is shown in Fig. 2. The resistivity increases with decreasing temperature, i.e., a semi-conducting behavior is predominant. At temperature of 71 K, a transition is observed on cooling. On heating this transition is shifted a little bit towards higher temperatures. After this temperature ($T \sim 74$ K) a metallic behavior is observed. This behavior is similar to electron or hole doped manganites [18–22]. A hysteresis between heating and cooling of $\rho(T)$ is characterized. The strontium deficiency leads to an increase in the value of $\rho(T)$ as well as a decrease in the electrical transition temperature. Because we deal with granular materials where there is a possibility to get more or less insulating barriers at the grain boundaries. These barriers will limit the residual resistivity. This mechanism is well known in ceramics, in ferrite as well as in high T_c superconductors where insulating barriers cause the appear-

Table 1
Lattice constants and Mn–O bond lengths of $Sm_{0.6}Sr_{0.4}MnO_3$

	a (Å)	b (Å)	c (Å)	Mn–O1 (Å)	Mn–O2 (Å)	Mn–O2 (Å)
Our sample	5.434(1)	7.681(2)	5.465(1)	1.934(25)	2.035(57)	1.819(57)
Sample of Ref. [10]	5.435	7.661	5.433	1.951	1.960	1.940

ance of Josephson junction below the transition temperature of the super-conducting grains. The difference in resistivity is still obtained with applying magnetic field on the sample during the heating and cooling measurements. The dependence of phase temperature on strontium concentration in $Sm_{1-x}Sr_xMnO_3$ was reported in different papers [9,12–14]. There is a transition, which occurred for $Sm_{0.6}Sr_{0.4}MnO_3$ single crystal at $T_c \sim 107$ K (see Ref. [9]) and at $T_c \sim 123$ K which is given in Ref. [14]. For the polycrystalline $Sm_{0.6}Sr_{0.4}MnO_3$ the transition temperature T_c is 125 K while T_p is 131 K [12]. It was reported by Martin et al. [13] that a transition to charge ordering phase occurred at $T_{CO} \sim 140$ K. From the above mentioned, in different works, the transition temperature is not the same for $Sm_{0.6}Sr_{0.4}MnO_3$. The crystal structure which is obtained from different works is the same for $Sm_{0.6}Sr_{0.4}MnO_3$. The lattice constants are identical but the oxygen atoms occupy different positions as a result of the tilt of the octahedron. The magnetic and electronic transport occur via oxygen atoms which construct this octahedron. This may lead to the difference in T_c. Also, the coexistence of the ferromagnetic, the canted antiferromagnetic, the charge and the orbital ordering leads to the appearance of the multicritical phase diagram. Looking at the resistivity–temperature dependence in our case (cooling run), one can note the transition from insulator to metallic behavior at $T \sim 74$ K. In the metallic state there are two transition temperatures at $T \sim 108$ K and $T \sim 157$ K. This may be attributed to the coexistence of charge and canted antiferromagnetic (weak ferromagnetic) ordering at 74 K $> T < 108$ K. The ferromagnetic ordering predominates at $T > 157$ K. Similar behavior was reported for $Sm_{0.5}Sr_{0.5}MnO_3$ where the coexisting correlations of the charge or orbital ordering, ferromagnetic and layered-antiferromagnetic ordering were observed [14].

The magnetoresistance (MR) of manganese perovskites can be of unprecedented magnitude. In most cases, the large resistance changes are achieved only in a strong magnetic field in the Tesla range, which severely limits their practical utility. Reducing the field scale and increasing the operating temperature has been the goal of a number of research groups world wide. The effect of external magnetic field on the resistivity behavior of $Sm_{0.6}Sr_{0.4}MnO_3$ compounds has been investigated. A decrease in resistivity with increasing the applied magnetic field on cooling as well as on heating runs is observed as shown in Figs. 3 and 4.

Variation of the resistivity of $Sm_{0.6}Sr_{0.4}MnO_3$ with temperature at different applied magnetic field (on both heating and cooling runs) shows that the transition becomes broader with applied field and shifts to higher temperatures. The decrease in the resistivity by the application of a magnetic field presumably is as a result of an increase in the ordering of the dipoles inside the samples. Generally, the sample requires higher transition energy to change from insulator to metal as justified by the broad transition. It seems that the transition on heating is sharp compared with that on cooling because on heating $Sm_{0.6}Sr_{0.4}MnO_3$ enters the metallic state faster than on cooling.

The increase of transition temperature (T_c) with increasing applied magnetic field is represented in Fig. 5. The value of T_c is determined by taking the first derivative of the resistivity with temperature at applied fields. As usual, the transition tem-
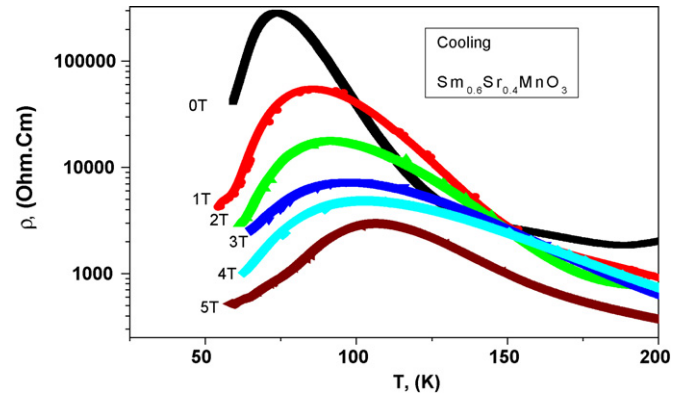

Fig. 3. Thermal dependence of the resistivity at applied magnetic fields of 0 T, 1 T, 2 T, 3 T, 4 T and 5 T of $Sm_{0.6}Sr_{0.4}MnO_3$ for cooling runs.
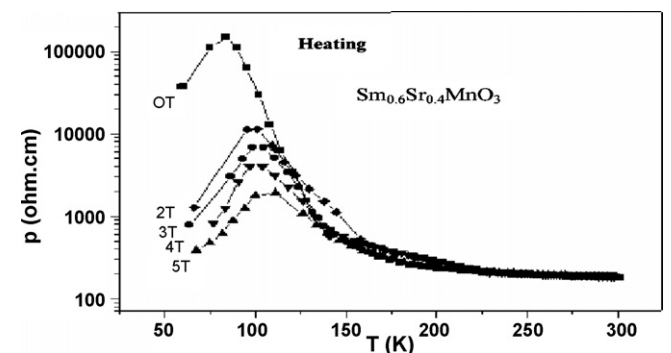

Fig. 4. Thermal dependence of the resistivity at applied magnetic fields of 0 T, 1 T, 2 T, 3 T, 4 T and 5 T of $Sm_{0.6}Sr_{0.4}MnO_3$ for heating runs.

perature increases with increasing the applied field. There is a difference in T_c on heating compared with that on the cooling cycle for $Sm_{0.6}Sr_{0.4}MnO_3$ sample (hysteresis) which increases from 8 K to 15 K with increasing magnetic field. Probably, the sample passes the phase border of metal to semiconductor faster on heating than on cooling. This may be due to a localization of the applied magnetic dipoles. Similar behavior was observed in $Sm_{0.65}Sr_{0.35}MnO_3$ by Borges et al. [23]. They observed a thermal hysteresis in the resistivity measurements of about 15 K between heating and cooling runs. We have a good agreement with the previous work at zero applied field.
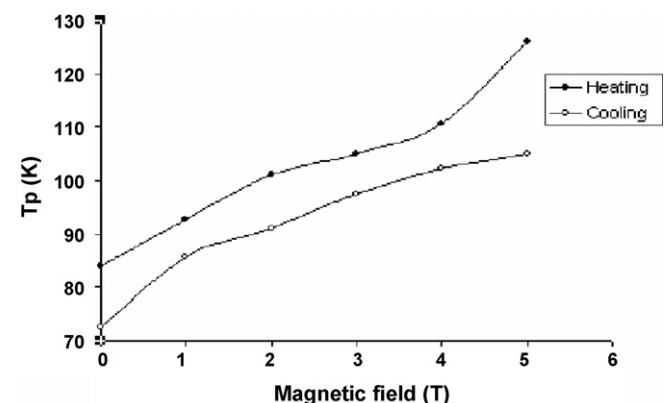

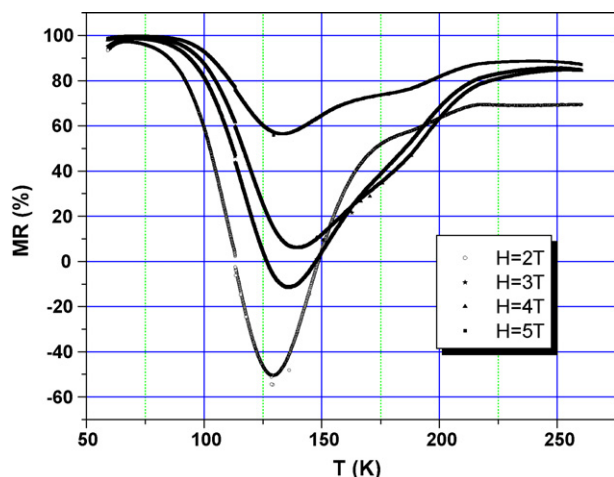Fig. 5. The variation of the transition temperature with applied magnetic field.

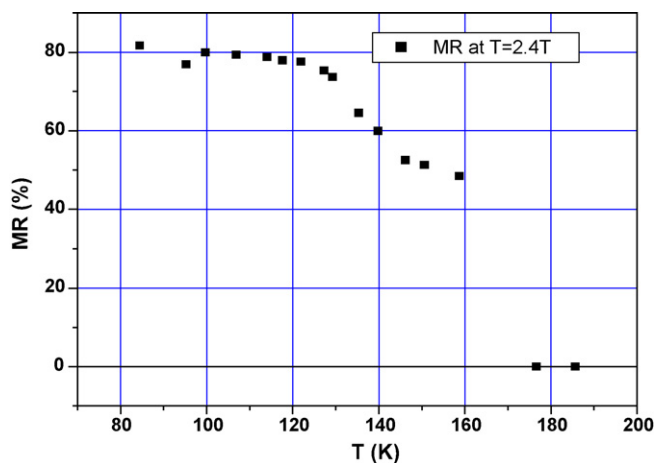Fig. 6. Magnetoresistance of $Sm_{0.6}Sr_{0.4}MnO_3$ at different applied magnetic fields.

Fig. 7. Magnetoresistance of $Sm_{0.6}Sr_{0.4}MnO_3$, of Ref. [10], at 2.4 T applied magnetic field.

Magnetoresistance of $Sm_{0.6}Sr_{0.4}MnO_3$ measured for different magnetic fields from 2 T up to 5 T is illustrated in Fig. 6. It is quite clear that CMR is observed at temperature of $T = 70$ K, MR values at magnetic fields 2 T, 3 T, 4 T and 5 T are 97%, 98.7%, 99.3% and 99.7%, respectively. The precedence in this work is the magnificent value of MR at $T = 260$ K (not so far from room temperature) where MR takes values 69.4% up to 87.3% for magnetic field from 2 T to 5 T, respectively. It is worthwhile to compare our MR measurements of $Sm_{0.6}Sr_{0.4}MnO_3$ with those reported by Dunaevsky et al. [10]. MR, reported in Ref. [10], of $Sm_{0.6}Sr_{0.4}MnO_3$ (at magnetic field 2.4 T) is shown in Fig. 7.

At $T = 84.4$ K, the MR, measured by Dunaevsky et al. [10] at $H = 2.4$ T, is 81.7% while our lies between 90.7% and 96.4%. In spite that both $Sm_{0.6}Sr_{0.4}MnO_3$ samples have the same structure (lattice constants are almost the same) and are prepared using solid-state reaction, they have different MR values. There is a difference in the thermal treatment during preparation and this

may lead to the difference in the tilt of octahedra. Moreover, as it is well known that the exchange interaction between Mn e_g and O 2p orbital is governed by the Mn–O1–Mn and Mn–O2–Mn angles, they are the basic parameters in the magnetic and electronic behaviors in this compound. So we have less distortion in the MnO_6 octahedra than that in Ref. [10] which leads to the increase in CMR value.

Acknowledgements

References

[1] M. Marezio, J. Remeika, P.D. Dernier, Acta Crystallogr. B 26 (1970) 2008.
[2] J.L. Garcia-Munoz, J. Rodriguez-Carvajal, Phys. Rev. B 46 (8) (1992) 4414.
[3] G.H. Jonker, J.H. Santen, Physica 16 (1950) 337.
[4] J.H. Santen, G.H. Jonker, Physica 16 (1950) 559.
[5] C. Zener, Phys. Rev. 82 (2) (1951) 403.
[6] A.R. Bishop, H. Roder, Cond-Mat/9703148, 1997, p. 1.
[7] H. Tanaka, T. Kawai, J. Appl. Phys. 88 (3) (2000) 1559.
[8] I.A. Abdel-Latif, A.S. Khramov, V.A. Trounov, O.P. Smirnov, Sh.Sh. Bashkirov, V.V. Parfenov, E.A. Tserkovnaya, G.G. Gumarov, Sh.Z. Ibragimov, Egypt. J. Solids 29 (2) (2006) 341.
[9] V.Yu. Ivanov, A.A. Mukhin, V.D. Travkin, A.S. Prokhorov, A.M. Balbashov, J. Magn. Magn. Mater. 258–259 (2003) 535.
[10] S.M. Dunaevsky, A.I. Kurbakov, V.A. Trounov, D.Yu. Chernyshov, V.V. Papov, V.V. Chernyshev, J. Roudriguez-Carvajal, Solid State Phys. (Fiz. Tverd. Tela) 40 (1998) 1271.
[11] D.Yu. Chernyshov, I.A. Kurbakov, V.A. Trounov, Physica B 276–278 (2000) 318.
[12] F. Damay, N. Nguen, A. Maignan, M. Hervieu, B. Raveau, Solid State Commun. 98 (1996) 997.
[13] C. Martin, A. Maignan, M. Hervieu, B. Raveau, Phys. Rev. B 60 (1999) 12191.
[14] Y. Tomioka, H. Hiraka, Y. Endoh, Y. Tokura, Phys. Rev. B 74 (2006) 104420.
[15] I.D. Luzyanin, V.A. Ryzhov, D.Yu. Chernyshov, A.I. Kurbakov, V.A. Trounov, A.V. Lazuta, V.P. Khavronin, I.I. Larionov, S.M. Dunaevsky, Phys. Rev. B 64 (2001) 094432.
[16] V.V. Runov, D.Yu. Chernyshov, A.A. Kurbakov, M.K. Runova, V.A. Trounov, A.I. Okorokov, J. Exp. Theor. Phys. 91 (5) (2000) 1017.
[17] V.B. Zlokazov, V.V. Chernyshev, J. Appl. Crystallogr. 25 (1992) 447.
[18] D. Grossin, J.G. Noudem, Solid State Sci. 6 (2004) 939.
[19] R.F.C. Marques, P.R. Abernethy, J.A.D. Matthew, C.O. Paiva-Santos, L. Perazolli, M. Jafelicci Jr., S.M. Thompson, J. Magn. Magn. Mater. 272–276 (2004) 1740.
[20] G. Li, G.-G. Hu, H.-D. Zhou, X.-J. Fan, X.-G. Li, Mater. Chem. Phys. 75 (2002) 101.
[21] I. Panagiotopoulos, N. Moutis, M. Ziese, A. Bollero, J. Magn. Magn. Mater. 299 (2006) 94.
[22] B.I. Belevtsev, A.Ya. Kirichenk, N.T. Cherpak, G.V. Golubnichay, I.G. Maximchuk, E.Yu. Beliayev, A.S. Panfilov, J. Fink-Finowicki, J. Magn. Magn. Mater. 281 (2004) 97.
[23] R.P. Borges, F. Ott, R.M. Thomas, V. Skumryev, J.M.D. Coey, J.I. Arnaudas, L. Ranno, Phys. Rev. B 60 (1999) 18.