

Provided for non-commercial research and educational use only.
Not for reproduction or distribution or commercial use.



Available online at
 ScienceDirect
www.sciencedirect.com

www.elsevier.com/locate/ssc

This article was originally published in a journal published by Elsevier, and the attached copy is provided by Elsevier for the author's benefit and for the benefit of the author's institution, for non-commercial research and educational use including without limitation use in instruction at your institution, sending it to specific colleagues that you know, and providing a copy to your institution's administrator.

All other uses, reproduction and distribution, including without limitation commercial reprints, selling or licensing copies or access, or posting on open internet sites, your personal or institution's website or repository, are prohibited. For exceptions, permission may be sought for such use through Elsevier's permissions site at:

<http://www.elsevier.com/locate/permissionusematerial>

Magnetic and photomagnetic studies in $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$

D. Bahadur^{a,*}, Saket Asthana^a, C. Carbonera^b, C. Desplanches^b, J.-F. Létard^b

^a Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology, Bombay, Powai, Mumbai-400076, India

^b Institut de Chimie de la Matière Condensée de Bordeaux, UPR CNRS 9048 - Université Bordeaux 1, Groupe des Sciences Moléculaires, 87 Av. Doc. A. Schweitzer, F-33608 Pessac, France

Received 22 December 2006; accepted 8 February 2007 by D.D. Sarma

Available online 13 February 2007

Abstract

We report magnetic and photomagnetic studies on polycrystalline $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$. Strong irreversibility in field cooled and zero field cooled data is observed. The hysteresis plot exhibits a very high coercivity at low temperatures. On photon irradiation, a decrease in the coercivity and an irreversible magnetization enhancement are observed. The analysis of all these data suggest that microscopic phase separation of competing ferromagnetism and antiferromagnetism and/or light-induced spin conversion processes among low, intermediate and high spin states of cobalt ions are responsible for all the properties.

© 2007 Elsevier Ltd. All rights reserved.

PACS: 75.30.Wx; 78.20.Ls; 74.25.Ha

Keywords: A. Cobaltates; D. Spin-state transitions; D. Photomagnetism; D. Electronic phase separation

1. Introduction

Hole doped perovskite manganites and cobaltates have been revisited in recent years due to their interesting magnetoelectronic properties ([1] and references therein). The magnetic properties, particularly, have received considerable attention due to electronic phase separation and competing coexisting phases [1–3]. Cobaltates, in addition, also exhibit variable spin states of cobalt with comparable energy scale. The consequences of this situation are the well studied thermally driven spin state transitions in LaCoO_3 and related systems [4–6] and stability of the unusual intermediate spin (IS) state for Co^{3+} ($t_{2g}^5 e_g^1$ with $S = 1$) and Co^{4+} ($t_{2g}^4 e_g^1$ with $S = 3/2$) in Sr- and Ca-substituted LaCoO_3 [6–8]. For investigating these two phenomena, a variety of methods have been adopted [7–10]. Photomagnetic effects are relatively unknown [11–14]. In fact, photomagnetism has been extensively studied in molecular complexes [15]. Of late, very interesting reports on photo-induced changes have appeared for several magnetic

oxide systems [16–18]. Amongst these, the most investigated recently are the perovskite oxides such as manganites of the type $\text{La}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$ [12] and $\text{Pr}_{0.6}\text{La}_{0.1}\text{Ca}_{0.3}\text{MnO}_3$ [13] or chromites, $\text{La}_{0.5}\text{Pr}_{0.5}\text{CrO}_3$ [17]. While for the hole doped manganites, most of the discussions are focussed on electronic phase separation of antiferromagnetic (AFM) and ferromagnetic (FM) phases and subsequent photo-induced growth of ferromagnetic phase, in cobaltates, on the other hand, these have been dealt with in terms of spin transitions also [2,11]. Seki et al. [19] have investigated the photomagnetic response of the thin films of Zn- and Ti-substituted NiFe_2O_4 and Al-substituted Fe_3O_4 , and the results have been interpreted in terms of a photo-induced inter valence charge transfer between the ions. A comparative study on thin films and bulk samples of $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$ has shown different efficiencies of photo-excitation [14].

The present studies deal with the compound $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$. There have been reports on the structural, electron transport and magnetic properties of the system, $\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3$ [20, 21]. Only preliminary studies have been done on the composition $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$. This compound, particularly, is expected to exhibit both the phenomena of electronic phase separation and spin transition. Another interesting facet of the present

* Corresponding author. Tel.: +91 22 25767632; fax: +91 22 25723480.

E-mail addresses: dhirenb@iitb.ac.in (D. Bahadur), letard@icmcb-bordeaux.cnrs.fr (J.-F. Létard).

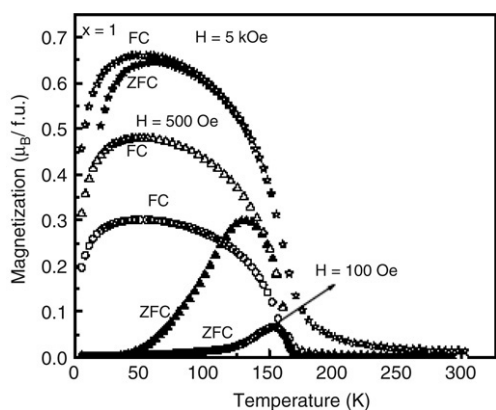


Fig. 1. Temperature dependence of magnetization (ZFC and FC) measured in different fields for sample $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$.

compound is the large orbital moments of Nd^{3+} ($L = 6$), that may induce a high anisotropy [22]. Also, for none of these compounds have photomagnetic studies been reported. In addition, the length scale of magnetically inhomogeneous phases may vary from sub nanometer to as large as a micrometer [3,23]. This may also bring in interesting time-dependent effects due to possible change in relative volume fraction of the competing phases as a function of external stimuli like temperature, magnetic field and photon excitation [3,21–24]. Herein, we report on the magnetic and photomagnetic properties of the compound $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$, to get an insight into the above-mentioned aspects.

2. Experimental section

Polycrystalline samples of $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ were synthesized through the citrate gel process. The as-prepared precursors were calcined at 1200°C in air for 6 h. The powder was then pelletized and sintered at 1300°C for 4 h. Having ascertained single phase formation through X-ray diffraction, we have carried out detailed magnetization, relaxation and photomagnetic studies via a coupled optical fibre to a Kr^+ laser (multi-line 647.1–676.4 nm) or a diode laser (830 nm) to the cavity of a MPMS-55 Quantum Design SQUID magnetometer. Measurements of magnetic moment versus intensity of the laser were carried out at 10 K and in a 2500 Oe field and between intensities of 0 and $25\text{ mW}/\text{cm}^2$.

3. Results and discussions

3.1. Magnetic studies

Fig. 1 shows the temperature dependence of zero-field cooled (ZFC) and field cooled (FC) magnetization measured in different magnetic fields of 100, 500 and 5000 Oe. Thermo-magnetic irreversibility behavior in ZFC and FC data is observed in all the three fields; the extent of irreversibility is more in lower fields. One of the reasons for this irreversibility is the frustration caused by competing FM and AFM interactions. Such behavior is common in the case of cobaltate and manganite based perovskites [1,22,23]. This is also characteristic of highly anisotropic compounds. In the

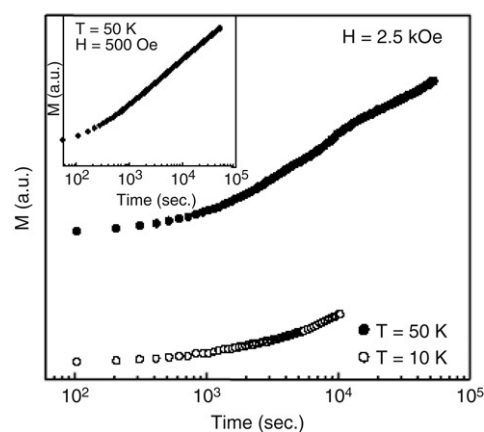


Fig. 2. Magnetization relaxation with time for $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ using a probing field of 2.5 kOe at 10 and 50 K. The inset shows the same behavior at 50 K in a 500 Oe field.

presence of local anisotropy, magnetic moments of the spins may be frozen in directions favored energetically. Alternately, if the system is cooled in the presence or absence of a field (FC, ZFC) and then the external field is applied, this may also lead to freezing of spins. These two competing effects possibly lead to the difference between M_{ZFC} and M_{FC} as a function of external applied field. The giant anisotropy may be on account of combination of properties of (1) Nd^{3+} ion with a large orbital angular momentum (L) value of 6 and (2) the IS state of Co^{3+} ($t_{2g}^5 e_g^1$) or Co^{4+} ($t_{2g}^4 e_g^1$), which are Jahn–Teller (J–T) ions. The larger spin–orbit coupling due to these ions and J–T distortion play a significant role in enhancing the anisotropy [20,22]. The J–T distortion leads to the buckling of the CoO_6 octahedra which also affects the magnetic and transport properties.

Both the FC and ZFC data measured in different fields exhibit a cusp with lowering of magnetization at lower temperatures implying AFM character within the sample besides the ferromagnetic one: a strong case for electronic phase separation. An alternative explanation for the drop in magnetization at lower temperatures could be on the basis of spin transitions. That is, as the temperature is lowered, high spin (HS) states get transformed to intermediate or low spin (LS) states depending upon the change in the crystal field splitting as compared to exchange energy [5–7].

We have studied the variation in magnetization with time at a constant field of 2.5 kOe and 500 Oe measured at 50 and 10 K for $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$, and this is shown in Fig. 2. The inset shows the long time relaxation behavior at a field of 500 Oe measured at 50 K. Most of such studies have been done at very low field up to a few Oe [25,26]. We have intentionally chosen a higher field of 2.5 kOe due to the features observed at this field in the magnetization curve reported later in this paper. Also, several recent reports on similar perovskites deal with high field studies [27,28]. The magnetization increases slowly with time, both at 10 and 50 K, with field values of 500 Oe and 2500 Oe.

The long time relaxation of magnetization is a strong indication of the frustrated behavior caused by competing FM and AFM phases leading to microscopic phase separation. Wu and Mitchell [29] reported such relaxation in Ca-, Sr-substituted

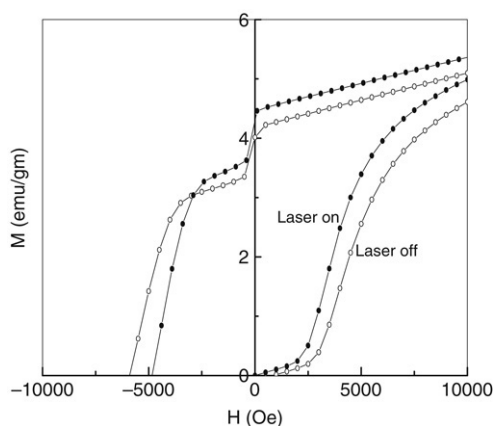


Fig. 3. Part of the plot of magnetization versus field with and without irradiation measured at 10 K and up to a field of 3 T.

Pr-manganite in an applied field up to 2 T and attributed it to the growth of FM phase, which is impeded by interface strain caused by competing AFM phases. These interfaces act as pinning centers for the growth of ferromagnetic domains. The implication of these interfaces could be generation of microscopic energy barriers which can be overcome by magnetic and thermal energies; their values at 2500 Oe and 10 K could be 0.015 and 0.8 meV respectively. Similar explanations have been put forward for several perovskite manganites in the recent past; the main focus of all these is the competing FM and AFM interactions and the evolution/growth of ferromagnetic domains at the expense of antiferromagnetic domains [27,28]. The present results can be discussed in terms of microscopic phase separation corresponding to AFM and FM phases with the possibility of a distribution of energies closely spaced due to the change in length scale and local structure causing slow growth of the ferromagnetic phase as a function of time at specific temperature and field. The origin of such microscopic magnetic phase separation could be related to magnetic inhomogeneities or local structural distortion leading to spontaneous phase separation with varying length scales [3,20].

3.2. Photomagnetic studies

We show in Fig. 3 a part of the hysteresis loop recorded at 10 K in a ZFC sample in the presence of laser irradiation and without it. Saturation is not observed up to an applied field of 3 T in either case. Under light irradiation, there is a significant change in the hysteresis behavior with regard to coercivity, remanence and magnetization at any point. The coercivity, which is remarkably high (~5895 Oe) without laser irradiation, drops with irradiation to a lower value (~4815 Oe). The origin of such a giant coercivity in oxide systems like this has been ascribed to the exchange bias phenomenon occurring at the interfaces of the phase-separated regions [30]. Furthermore, the large local anisotropy induced by high orbital angular momentum of Nd^{3+} ion as well as of J–T ions as discussed above could be the possible reasons for the high coercivity. The reduction in coercivity, on irradiation, can be attributed to the reduction of concentration of J–T

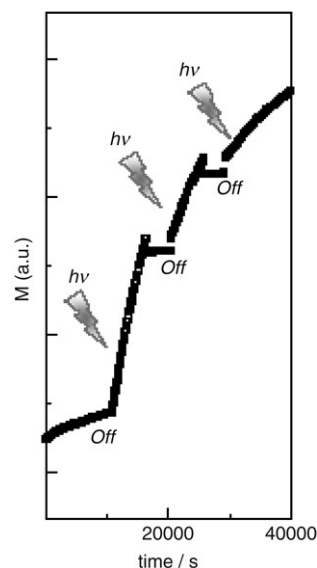


Fig. 4. The variation of magnetization as a function of time measured at 10 K and in a field of 2500 Oe. The region marked with an arrow is with irradiation, while the region marked with “off” is without irradiation.

ions. A second interpretation could be on the basis of ionic size variation of Co^{3+} ion in different spin states. The ionic size varies as $r_{\text{Co(HS)}} > r_{\text{Co(IS)}} > r_{\text{Co(LS)}}$. Therefore, the CoO_6 octahedra gets more symmetric as the population of HS state increases with light which favors the double-exchange interactions between neighboring sites. As a result, the spins may get aligned easily, which in turn decreases the H_c value in the presence of light. In either of the interpretations, spin transformation is a prerequisite.

On irradiation, the magnetization at any field is higher in all the quadrants except the fourth. In the fourth quadrant, however, the magnetization drops sharply. Another interesting feature of the hysteresis plot is a sudden change in the slope of the magnetization value at a field of 2500 Oe. This feature has striking resemblances to several recent work [11,28,30] on such perovskites, dealt with and understood on the basis of electronic phase separation. The initial increase has generally been attributed to alignment of the FM regions in the sample and the sudden slope change at 2500 Oe could be due to the conversion of AFM phase into FM phase in the magnetically inhomogeneous system, as also proposed by Zhang et al. [11].

The hysteresis plot exhibits a clear distinction between irradiated and non-irradiated curve above a field of 2000 Oe. In view of this, we have chosen a field of 2500 Oe at which the photo-induced studies have been carried out after the sample was zero-field cooled. These studies were done at the two sets of wavelengths with an intensity of 5 mW/cm^2 to ensure the minimization of thermal effects. The main features of these results carried out at 647.1–676.4 nm are presented in Fig. 4.

There is a very slow increase in magnetization without light irradiation measured up to approximately three hours as also seen in Fig. 2. The illumination has a strong influence on the behavior. A significant rise in magnetic moment is observed with irradiation in the next about an hour. Following this, as the irradiation is switched off, the magnetic moment reduces

by a very small amount and remains essentially constant with time until the light is switched on again after approximately another hour. We argue that this small drop may be on account of the thermal effects which repeat the next time when the irradiation is switched off. This also indicates that at 10 K the lifetime of the photo-induced state is at least in the range of an hour. Further, it rules out the thermal effects as the reason for increase in magnetic moments. The large increase in moments is seen at each stage of irradiation. However, there is a change in slope and a tendency to saturation is observed in the last set of photo-excitation experiment in Fig. 4. It is worth mentioning here that if the sample is irradiated by a laser with a wavelength of 830 nm, the change in magnetic moment as a function of time is very small. On the basis of all these experiments and particularly as illustrated by Fig. 4, the thermal effects cannot explain the magnetic behavior. A more realistic explanation could be based on the field-induced spin transitions. Co^{3+} and Co^{4+} are known to exist/coexist in low, intermediate and high spin states in these cobaltates [7, 8]. The flexibility in the spin state adopted by the Co ions is a consequence of the comparable energies of the Hund's rule exchange energy (E_{ex}) and crystal field splitting (Δ_{CF}) meaning that the low spin (LS), intermediate spin (IS) and high spin (HS) states may exist/coexist for Co^{3+} and Co^{4+} ions in cobaltates and may be easily driven from one state to another using different sources of energy. Extensive literature exists on the studies of such spin transitions ([5] and references therein). However, reports on photo-induced transitions particularly in cobaltates are very few [2,11]. Roy and Ali [2] have observed photo-induced spin transitions from the intermediate spin state of Co to the high spin state in $\text{GdBaCo}_2\text{O}_5$. Similarly, Zhang et al. [11] reported a photo-induced spin transition of the Co^{3+} ion from the low spin ($t_{2g}^6 e_g^0$) to the high spin ($t_{2g}^4 e_g^2$) or intermediate spin ($t_{2g}^5 e_g^1$) state in $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_{1.8}\text{Co}_{0.2}\text{O}_7$. A photo-induced spin transition has also been reported in $\text{La}_{0.5}\text{Sr}_{0.5}\text{CrO}_3$ [31], where the authors have used the electron paramagnetic resonance (EPR) technique to observe the photo-excitation of the t_{2g} electron to the e_g state for Cr^{3+} ($3d^3$) which is isoelectronic with Mn^{4+} . It is noteworthy that the transition shown in Fig. 4 is consistent with the above reports and is similar to Light-Induced Excited Spin State Trapping (LIESST) phenomena reported in molecular systems [15], in which the two spin states are represented by two potential wells separated by an activation energy barrier. One may argue in the favor of microscopic phase separation as discussed earlier in the text and possible growth of ferromagnetic domains at the expense of antiferromagnetic domains on light irradiation. This will, however, require a reversible transition as the irradiation is switched off. Hence, we suggest that the small drop seen in the magnetization at each stage in the light off mode consists of contributions both from thermal as well as FM/AFM domain reversibility. To confirm this, we also did some preliminary experiments on photo-induced effects on the compound $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$, and we did not observe any jump in magnetization as observed in case of $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$. This would be expected as manganites exhibit only phase separation and not a spin transition. It may be noted, however, that

the compound $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ did show the time-dependent effects similar to Fig. 2.

We have also studied the influence of the intensity of laser on the enhancement of moment at 4 kOe at 10 K (not shown here). The moment increases initially very slowly up to an applied intensity of 10 mW cm^{-2} and then increases rather sharply if the applied intensity is increased to 25 mW cm^{-2} . The intensity of irradiation is directly proportional to the number of photons. As the number of photons irradiating the sample increases, more and more low and intermediate spin states get transformed to high spin states. The energy required for spin transitions in these cobaltates may range between 0.65 eV for the LS–IS transition and 2.3 eV for the LS–HS transition [11], while the energy corresponding to the 647.1–676.4 nm and 830 nm laser beams correspond to ~ 1.91 – 1.83 eV and 1.49 eV, respectively. The present results can be understood on the basis of significant fraction of LS/IS state of Co^{3+} and Co^{4+} at temperatures < 50 K which, in the presence of irradiation, can slowly transform to HS states with higher magnetic moment. The extent of transformation would depend upon the intensity and time.

4. Conclusion

Magnetic and photomagnetic studies on the compound $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ exhibit the following important features: (a) strong irreversibility in FC and ZFC magnetization data, (b) long time relaxation of magnetization with an applied field up to 2.5 kOe and (c) a significant increase in magnetization and decrease in coercivity under photon irradiation.

Magnetic studies without light irradiation are understood in the framework of microscopic phase-separated ferromagnetic and antiferromagnetic regions with varying length scales, the ratio of which can be varied by changing temperature or other conditions as they are energetically close to each other. Photomagnetic studies, on the other hand, suggest spin transitions from low/intermediate to high spin states of cobalt as the major cause of the effects. Both the spin transitions and magnetic frustration caused by competing ferromagnetic and antiferromagnetic interactions seem to play a strong role in explaining all the features of the present results. Spin transitions can be explained by an asymmetric double well as extensively discussed in the case of spin crossover systems in molecular complexes. Therefore, we conjecture that the energy barrier may be very small and distributed in the case of coexisting FM and AFM phases with varying length scales, and this can be easily overcome by thermal and magnetic energies available. For the spin transitions, however, the barrier height in the asymmetric double well may be large and can be achieved by photon irradiation. A change in magnetic properties on photon irradiation is of particular importance in the development of magneto-optical memories.

Acknowledgements

This work was supported in part by the LAFICS program. The authors would like also to thank the network of excellence

MAGMANet [FP6-515767-2] and the Aquitaine Region for supporting the photomagnetic platform. Thanks are also due to DST, Government of India, for support.

References

- [1] C.N.R. Rao, B. Raveau, Colossal Magneto Resistance, Charge Ordering and Related Properties of Manganese Oxides, World Scientific, Singapore, 1998.
- [2] S. Roy, N. Ali, Solid State Commun. 128 (2003) 91.
- [3] V.B. Shenoy, D.D. Sarma, C.N.R. Rao, Chem. Phys. 7 (2006) 2053.
- [4] K. Asai, P. Gehring, H. Chou, G. Shirane, Phys. Rev. B 40 (1989) 10982.
- [5] C.N.R. Rao, Md.M. Seikh, C. Narayana, in: P. Gütllich, H.A. Goodwin (Eds.), Topics in Current Chemistry, V234, 2004, pp. 1–21.
- [6] P.M. Raccach, J.B. Goodenough, Phys. Rev. 155 (1967) 932.
- [7] P. Ravindran, H. Fjellvåg, A. Kjekshus, P. Blaha, K. Schwarz, J. Luitz, J. Appl. Phys. 91 (2002) 291.
- [8] D. Bahadur, S. Kollali, C.N.R. Rao, M.J. Patni, C.M. Srivastava, J. Phys. Chem. Solids 40 (1979) 981.
- [9] Y.K. Tang, Y. Sun, Z.H. Cheng, J. Appl. Phys. 100 (2006) 023914.
- [10] A. Chainani, M. Mathew, D.D. Sarma, Phys. Rev. B 46 (1992) 9976.
- [11] R.L. Zhang, J.M. Dai, W.H. Song, Y.Q. Ma, J. Yang, J.J. Du, Y.P. Sun, J. Phys.: Condens. Matter 16 (2004) 2245.
- [12] H. Huhtinen, R. Laiho, E. Lähderanta, L.S. Vlasenko, M.P. Vlasenko, V.S. Zakhvalinskii, Phys. Rev. B 62 (2000) 11614.
- [13] M. Baran, S.L. Gnatchenko, O.Yu. Gorbenko, A.R. Kaul, R. Szymczak, H. Szymczak, Phys. Rev. B 60 (1999) 9244.
- [14] O. Yanagisawa, M. Izumi, K.-H. Huang, W.-Z. Hu, Y. Shen, K. Nakanishi, Y. Takahashi, N. Nojima, J. Magn. Mater. 211 (2000) 133.
- [15] P. Gütllich, H.A. Goodwin, Spin Crossover in Transition Metal Compounds, vols. I–III, in: Topics in Current Chemistry, Springer, Berlin, 2003.
- [16] Y. Muraoka, H. Tabata, T. Kawai, Solid State Commun. 120 (2001) 255.
- [17] M. Arai, T. Odagiri, O. Yanagisawa, M. Izumi, Solid State Electron. 47 (2003) 2187.
- [18] A.K. Giri, K. Pellerin, W. Pongsaksawas, M. Sorescu, S.A. Majetich, IEEE Trans. Magn. 36 (2000) 3029.
- [19] M. Seki, A.K.M. Akther Hossain, T. Kawai, H. Tabata, J. Appl. Phys. 97 (2005) 083541; M. Seki, A.K.M. Akther Hossain, H. Tabata, T. Kawai, Solid State Commun. 133 (2005) 791.
- [20] D.D. Stauffer, C. Leighton, Phys. Rev. B 70 (2004) 214414.
- [21] K. Yoshi, H. Abe, Phys. Rev. B 67 (2003) 094408.
- [22] S. Asthana, A.K. Nigam, D. Bahadur, J. Appl. Phys. 97 (2005) 10C101.
- [23] V.V. Sikolenko, A.P. Sazonov, I.O. Troyanchuk, T. Tobbens, U. Zimmermann, E.V. Pomjakushina, H. Szymczak, J. Phys.: Condens. Matter 16 (2004) 7313.
- [24] H. Kuwahara, Y. Tomioka, A. Asamitsu, Y. Moritomo, Y. Tokura, Science 270 (1995) 961.
- [25] D.N.H. Nam, K. Jonason, P. Nordblad, N.V. Khiem, N.X. Phuc, Phys. Rev. B 59 (1999) 4189.
- [26] R.S. Freitas, L. Ghivelder, F. Damay, F. Dias, L.F. Cohen, Phys. Rev. B 64 (2001) 144404.
- [27] A. Anane, J.-P. Renard, L. Riversat, C. Dupas, P. Villet, M. Viret, L. Pinsard, R. Revolevschi, Phys. Rev. B 59 (1999) 77.
- [28] V. Hardy, A. Maignan, S. Hébert, C. Yaïcle, C. Martin, M. Hervieu, M.R. Lees, G. Rowlands, D.Mc.K. Paul, B. Raveau, Phys. Rev. B 68 (2003) 220402.
- [29] T. Wu, J.F. Mitchell, Phys. Rev. B 69 (2004) 100405.
- [30] Y.-K. Tang, Y. Sun, Z.H. Cheng, J. Appl. Phys. 100 (2006) 23914.
- [31] M. Arai, T. Odagiri, O. Yanagisawa, M. Izumi, Solid State Electron. 47 (2003) 2187.