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SCHOTTKY-LIKE ANOMALY IN THE LOW-TEMPERATURE SPECIFIC HEAT OF POLYCRYSTALLINE $Y_{0.3}Gd_{0.2}Sr_{0.5}MnO_3$

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Abstract. In this paper we have synthesis of a sample of $Y_{0.3}Gd_{0.2}Sr_{0.5}MnO_3$ by solid state ceramic route method. The structural and thermodynamic properties of polycrystalline samples of $Y_{0.3}Gd_{0.2}Sr_{0.5}MnO_3$ were measured in order to investigate the effect of higher magnetic moment ion Gd and divalent Sr over Y ion. The structural transition from hexagonal to orthorhombic is observed at very high doping of Gd ion. Low temperature specific heat measurements were performed at 2-300 K at three different applied magnetic fields, which reveals the signature of Schottky-like anomaly in the present sample.

1. Introduction

Now a days ,multiferroic materials are attracting a lot of interest because of their tremendous applications in microwave devices [1], high density data storage [2] and sensor devices [3]. Multiferroics are a class of materials that posses two or more ferroic properties (i.e. ferromagnetism, ferroelectricity and ferroelectricity) in the single phase. This means that these materials contains spontaneous magnetization that can be reoriented by an applied magnetic field, spontaneous polarization that can be reoriented by applied electric field and spontaneous deformation, that can be reoriented by an applied stress [4-6]. Research into Multiferroic materials has increased dramatically in recent years [7-9]. A number of new rare-earth oxides have been shown to exhibit a coupling between magnetic and electric phases. Therefore understanding the physics behind these class of material is an essential gateway to explore more interesting features and phenomenon such as spin glass [10] and charge ordering [11]. Effect of magnetic field [12] and suitable doping on multiferroics can change the orientation of spins [7]. It was studied that application of magnetic field can also alter the physical properties of the material such as structure, heat capacity and magnetic properties [13]. Therefore the application of magnetic field over the material is taken as a tool to study the spin exchange mechanism.

Multiferroic materials are generally perovskite structure of $RMnO_3$; where R is a rare earth material (Gd to Lu, Y, Sc). Depending on the rare earth ionic size $RMnO_3$ (R=Gd to Lu, Y, Sc) crystallize into either orthorhombic or hexagonal phase [14]. That means compositions over A site (in ABO_3) or the ionic radii of A site can alter the structure from orthorhombic to hexagonal. Hexagonal $YMnO_3$ is a well studied system [15, 16], where non magnetic Y plays an important role in exchange interaction [17]. Several attempts were made to see the effect of

externally applied magnetic field, pressure, temperature over $YMnO_3$ [18, 19]. There were many efforts were made to increase Neel temperature of this materials. It is very interesting to understand the effect of higher magnetic moment ion such as Gd and simultaneously divalent Sr on $YMnO_3$. In this present paper we explore the doping of paramagnetic Gd and Sr over Y ion.

2. Experimental details

Polycrystalline sample of $Y_{0.3}Gd_{0.2}Sr_{0.5}MnO_3$ was prepared by the standard solid-state ceramic route. Considering the hygroscopic nature of the rare earth material Y_2O_3, Gd_2O_3, $SrCO_3$ and MnO_2, they were given pre-heat treatment at 1000 ºC for 10 hours. The obtained powder is regrind and compressed in to pellets of 10 mm diameter and 1.5 mm thickness by applying a pressure of 3-4 tons per square inch. The pellets were sintered at 1350 ºC for 24 hours. The room temperature XRD pattern was measured by a Rigaku Dmax 300 diffractometer using the CuKα radiation. Grain size micrographs of fractured surface was taken by SEM and heat capacity measurements by SQUID PPMS systems under three different applied magnetic fields 0 T, 5 T, 8 T within the temperature range of 2 K-300 K.

3. Results and discussions

3.1. Structural analysis. In $YMnO_3$, the structure is pure hexagonal Imma space group [20]. Hopefully with the doping with high magnetic moment material as Gd in our system, there must be a structural transition from hexagonal to orthorhombic structure. To confirm of the same, we took the XRD pattern of the sample $Y_{0.3}Gd_{0.2}Sr_{0.5}MnO_3$ which is shown in Fig. 1.

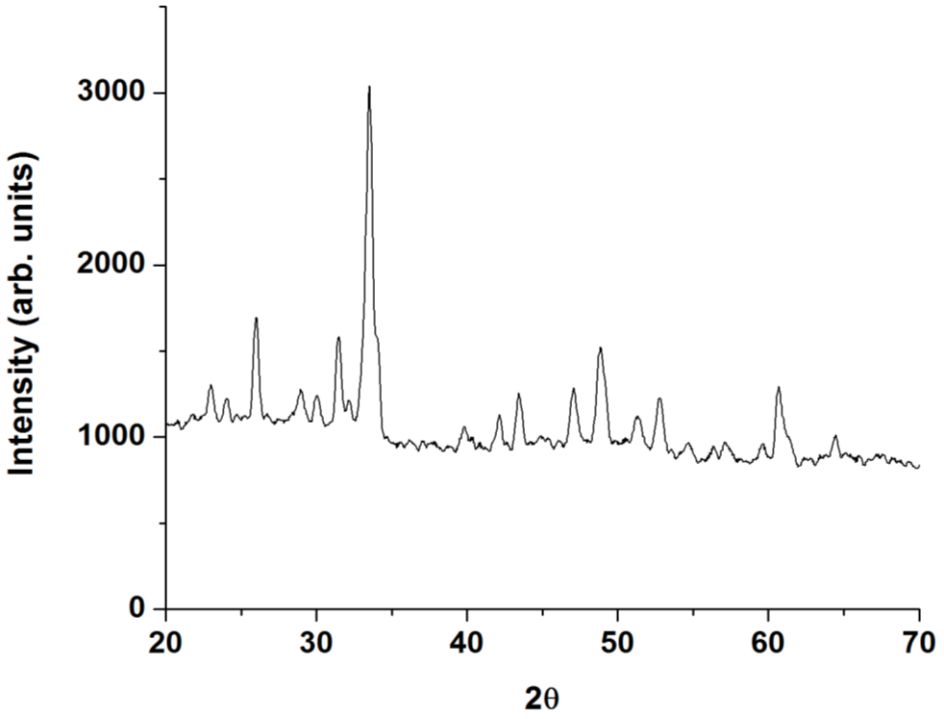


Fig. 1. X-ray diffraction measurement of $Y_{0.3}Gd_{0.2}Sr_{0.5}MnO_3$ showed mix phase with orthorhombic and hexagonal phase.

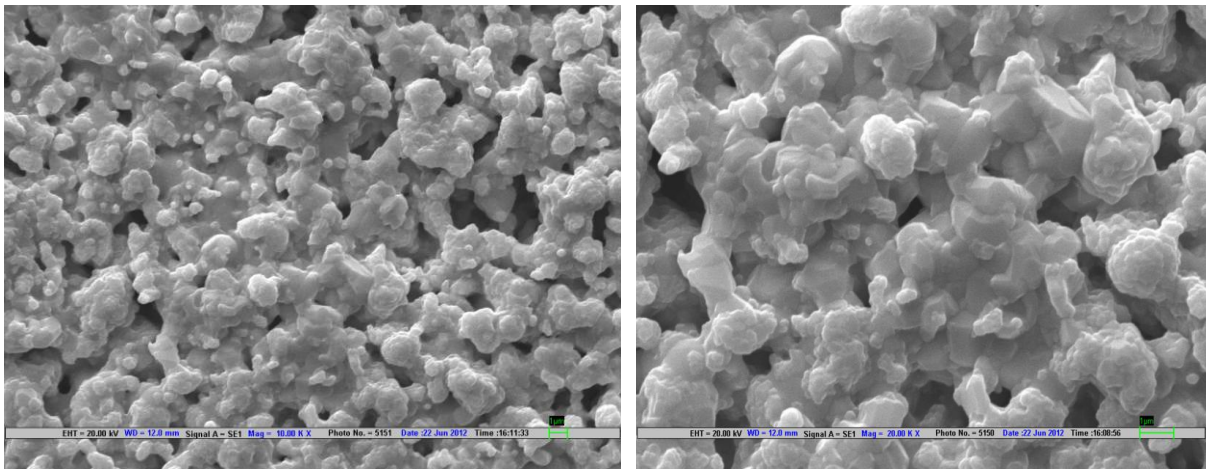
The structure of the sample detected was orthorhombic with Pbnm space group with some structural distortion towards hexagonal phase. Mix phase with orthorhombic and hexagonal phase, which is verified with X'pert plus suite. It is noted that the small fraction of

doping with Gd and Sr over Y led to structural distortion. Dependence of structural distortion on the sintering temperature has been reported by Liu et al. [21]. We estimated the average particle size by using Debye-Scherrer formula [22]:

$$L = \frac{0.9\lambda}{\beta\cos\theta} \ ,$$

where 'λ' is wave length of X-Ray (0.1541 nm), 'β' is FWHM (full width at half maximum) and 'θ' is the diffraction angle. The average particle size by the above mentioned method was found around 7 nm.

3.2. SEM measurement. Figure 2(a), (b) shows scanning electron microscopy (SEM) of the fractured surface provided further insight into the morphology and grain size details of the sample $Y_{0.3}Gd_{0.2}Sr_{0.5}MnO_3$. The prepared sample shows a compact distribution over the surface and good connectivity between grains. It shows a flake-type formation with particle size distribution about 15 nm. The morphology of the particles is generally spherical, but the bare particles have some big agglomerates.



(a) (b)

Fig. 2. SEM micrograph of fractured surface of $Y_{0.3}Gd_{0.2}Sr_{0.5}MnO_3$ shows the average grain size with XRD particle size.

3.3. Heat capacity analysis. Figure 3 shows the low temperature specific heat (LTSH) of YGSMO under 0 T, 1 T and 8 T magnetic fields. A high value of specific heat at lower temperatures is observed in contrast to insulating manganites like $La_{0.8}Ca_{0.2}MnO_3$ [23]. Similar high values of specific heat have been observed in $Dy_{0.5}Ca_{0.5}MnO_3$ studied by Lopez et al. [24].Under zero magnetic field, the low temperature specific heat shows a significant shoulder at about 10K which is shown in the inset of Fig. 3 . While the unusual feature in LTSH becomes indistinctive gradually with the increase in magnetic fields, a hump is still distinguishable even under magnetic field H=8 T which is shown in the inset of Fig. 3. As can be seen from Fig. 3, the specific heat below 15 K has a strong Schottky-like anomaly. Probably the existence of the Schottky anomaly is related with the Kramer's theorem. It states that an ion possessing an odd number of electrons, no matter how unsymmetrical the crystal field, must have a ground state that is at least doubly degenerate [25]. This could lead to the thermal depopulation that produces the Schottky anomaly in the specific heat. Ions of Ce, Nd, Sm, Gd, Dy, Er, and Yb all have an odd number of electrons and their respective oxides present a Schottky anomaly in the specific heat. However, the Kramers theorem does not exclude that ions with an even number of electrons might also have a doubly degenerate ground state.

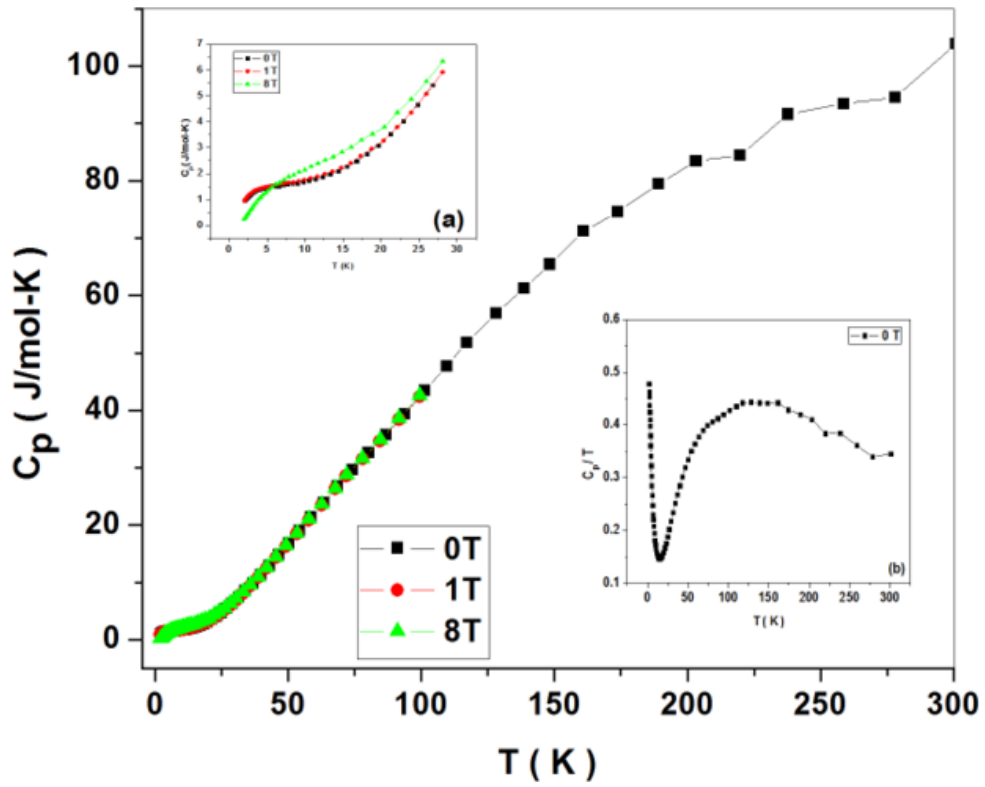


Fig. 3. Low temperature specific heat measurement of $Y_{0.3}Gd_{0.2}Sr_{0.5}MnO_3$ showed Schottky-like anomaly in the low temperature region.

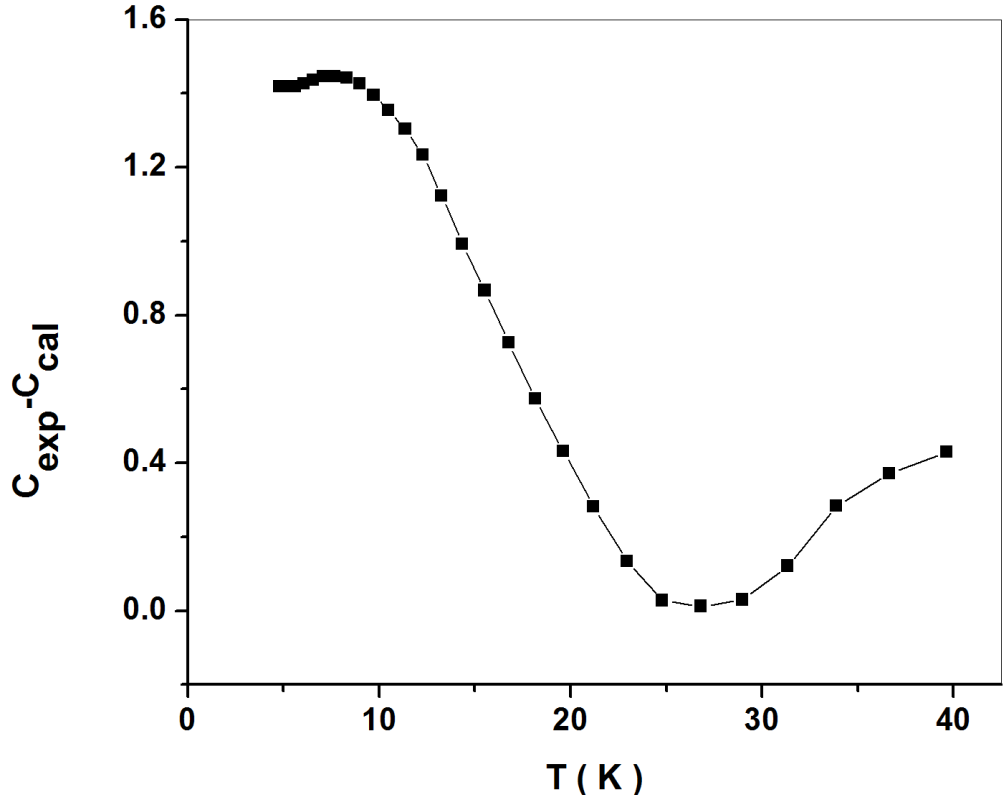


Fig. 4. Differece plot of specific heat of background data $La_{0.7}Pb_{0.3}MnO_3$ and $Y_{0.3}Gd_{0.2}Sr_{0.5}MnO_3$ gives the excess contributions C (T) to the specific heat at low temperature.

In order to get an idea of these anomalies, we have subtracted a suitable background from the measured data for YGSMO. As a background, we used specific-heat data for $La_{0.7}Pb_{0.3}MnO_3$ [26]. $La_{0.7}Pb_{0.3}MnO_3$ is a ferromagnetic metallic manganite, which has specific-heat contributions from electronic excitations and spin waves at low temperatures, but it has no anomalies related to rare-earth 4f electrons or glassy magnetic behavior. Therefore, the data for $La_{0.7}Pb_{0.3}MnO_3$ yield a background estimate to the maximum in the low temperature region, which helps to appreciate the magnitude of the anomalies in the specific heat of YGSMO.

The difference plot shown in Fig. 4 gives qualitative information on the excess contributions C (T) to the specific heat at low temperature. The main feature is a prominent wide peak below 25 K, which should be associated with a Schottky-like anomaly caused by crystal-field level excitations of 4f electronic states in the Gd ions. The re-increase above 25 K may be related to the spin-glass ordering.

For manganites the basic contributions to the specific heat in the low temperature range can be described by [27]:

$$C = \beta_{3/2}T^{3/2} + \gamma T + B_3T^3 + B_5T^5. \quad (1)$$

Here, $\beta_{3/2}$ is the coefficient of the contribution from spin wave excitations for ferromagnetic order, γ is the coefficient of the electronic specific heat, B_3 and B_5 are coefficients of the contribution from the lattice. The best range for the fitting according to equation (1) has been found to be 20–40 K. For this temperature range nuclear hyperfine effects in the specific heat need not be considered, as they contribute appreciably only at much lower temperature T < 2 K. From B_3 we calculate the Debye temperature (θ_D), $\theta_D = (12\pi^4 pR/5B_3)^{1/3}$ where R is the gas constant and p is the number of atoms in each molecule The results of the fitting by Equation (1) are shown in the Fig. 5 and the parameters obtained are shown in Table 1. The results are in good agreement with these kind of manganites [28].

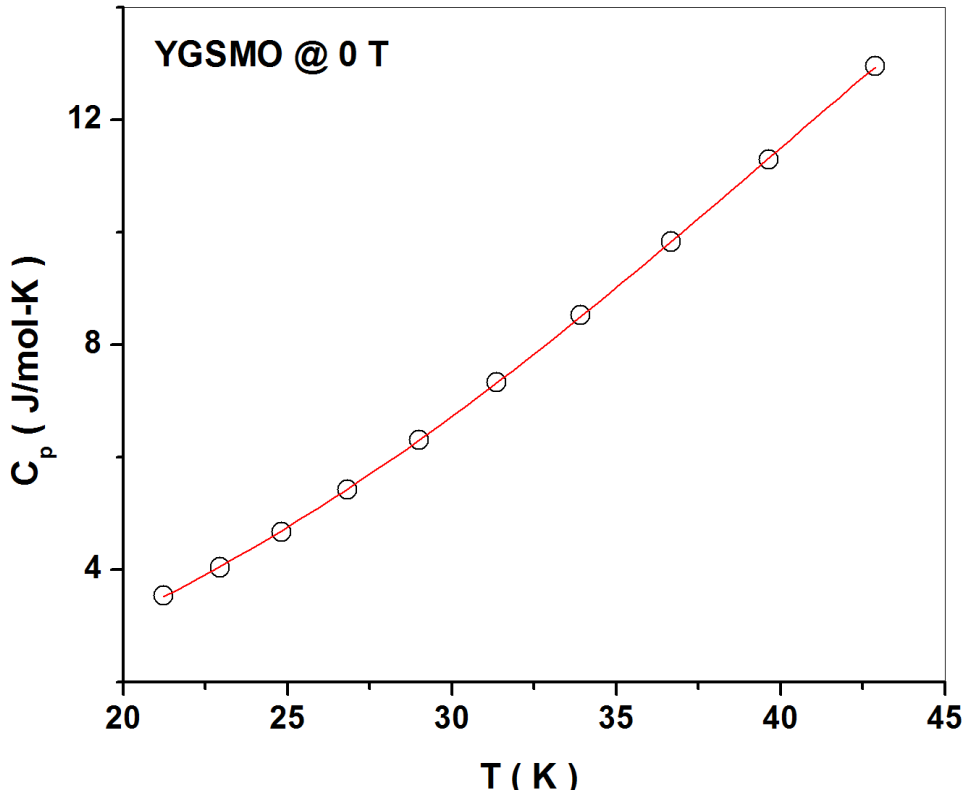


Fig. 5. Linear fitting by Equation (1).

Table 1. Fitting parameter for YGSMO.

Sample	$\beta_{3/2}$, mJ mol^{-1} K$^{-5/2}$	γ, mJ mol^{-1} K^{-2}	B_3, mJ mol^{-1} K^{-4}	B_5, mJ mol^{-1} K$^{-6}\times10^{-3}$	θ_D, K
YGSMO	7.21	67.73	0.16	-0.03	392.79

4. Conclusions

Polycrystalline $Y_{0.3}Gd_{0.2}Sr_{0.5}MnO_3$ orthorhombic sample was prepared by standard solid state ceramic route method and mix phase is confirmed with X ray studies and reveals the obvious shift of structure towards hexagonal phase to orthorhombic phase. This is due to the disorder of higher magnetic moment ions which we introduced at R site. The low temperature specific heat was investigated and Schottky-like anomaly was found.

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References

[1] Xiao-Yu Zhang, Xuan-Cong Wang, Feng Xu, Yun-Gui Ma, C.K. Ong *// Review of Scientific Instruments* **80(11)** (2009) 114701.
[2] J.F. Scott *// Nature Materials* **6(4)** (2007) 256.
[3] M. Vopsaroiu, M.G. Cain, G. Sreenivasulu, G. Srinivasan, A.M. Balbashov *// Materials Letters* **66(1)** (2012) 282.
[4] Y. Yamasaki, S. Miyasaka, Y. Kaneko, J.-P. He, T. Arima, Y. Tokura *// Physical Review Letters* **96(20)** (2006) 207204.
[5] Jacek C. Wojdeł, Jorge Íñiguez *// Physical Review Letters* **103(26)** (2009) 267205.
[6] Jacek C. Wojdeł, Jorge Íñiguez *// Physical Review Letters* **105(3)** (2010) 037205.
[7] W. Eerenstein, N.D. Mathur, J.F. Scott *// Nature* **442(7104)** (2006) 759.
[8] D.I. Khomskii *// Nature Communications* **3** (2013) 904.
[9] Sang-Wook Cheong, M. Mostovoy *// Nature Materials* **6(1)** (2007) 13.
[10] S. Petit, F. Moussa, M. Hennion, S. Pailhès, L. Pinsard-Gaudart, A. Ivanov *// Physical Review Letters* **99 (26)** (2007) 266604.
[11] Bas B. Van Aken, Thomas T.M. Palstra, Alessio Filippetti, Nicola A. Spaldin *// Nature Materials* **3(3)** (2004) 164.
[12] Minjung Kim, Harini Barath, Xiaoqian Chen, Young-Il Joe, Eduardo Fradkin, Peter Abbamonte, S. Lance Cooper *// Advanced Materials* **22(10)** (2010) 1148.
[13] N. Pavan Kumar, G. Lalitha, P. Venugopal Reddy *// Physica Scripta* **83(4)** (2011) 045701.
[14] Shintaro Ishiwata, Yusuke Tokunaga, Yasujiro Taguchi, Yoshinori Tokura *// Journal of the American Chemical Society* **133(35)** (2011) 13818.
[15] P.A. Sharma, J.S. Ahn, N. Hur, S. Park, Sung Baek Kim, Seongsu Lee, J.-G. Park, S. Guha, S-W. Cheong *// Physical Review Letters* **93(17)** (2004) 177202.
[16] A. V. Goltsev, R. V. Pisarev, Th. Lottermoser, M. Fiebig *// Physical Review Letters* **90(17)** (2003) 177204.
[17] D.-Y. Cho, J.-Y. Kim, B.-G. Park, K.-J. Rho, J.-H. Park, H.-J. Noh, B. J. Kim, S.-J. Oh, H.-M. Park, J.-S. Ahn, H. Ishibashi, S-W. Cheong, J.H. Lee, P. Murugavel, T.W. Noh, A. Tanaka, T. Jo *// Physical Review Letters* **98(21)** (2007) 217601.
[18] H. Lueken *// Angewandte Chemie* **47(45)** (2008) 8562.

[19] LI Na, LIN Fang-ting, MA Xue-ming, SHI Wang-zhou *// Guang Pu Xue Yu Guang Pu Fen Xi / Spectroscopy and Spectral Analysis* **28(3)** (2008) 606.
[20] Tapan Chatterji, Bachir Ouladdiaf, Paul F Henry, Dipten Bhattacharya *// Journal of Physics: Condensed Matter* **24**(33) (2012) 336003.
[21] Sheng-Hsu Liu, Jung-Chun-Andrew Huang, Xiaoding Qi, Wei-Jui Lin, Yu-Jhan Siao, Chun-Rong Lin, Jin-Ming Chen, Mau-Tsu Tang, Yu-Hua Lee, Jung-Chuan Lee *// AIP Advances* **1** (2011) 032173.
[22] B.D. Cullity, *Elements of X Ray Diffraction* (BiblioBazaar, 2011).
[23] J.J. Hamilton, E.L. Keatley, H.L. Ju, A.K. Raychaudhuri, V.N. Smolyaninova, R.L. Greene *// Physical Review B* **54(21)** (1996) 14926.
[24] J. López, O.F. de Lima, P.N. Lisboa-Filho, F.M. Araujo-Moreira *// Physical Review B* **66(21)** (2002) 214402.
[25] N.W. Ashcroft, N.D. Mermin, *Solid State Physics* (Philadelphia, Saunders College Publishing, 1976).
[26] Nilotpal Ghosh, Suja Elizabeth, H.L. Bhat, U.K. Rößler, K. Nenkov, S. Rößler, K. Dörr, K.-H. Müller *// Physical Review B* **70(18)** (2004) 184436.
[27] B.F. Woodfield, M.L. Wilson, J.M. Byers *// Physical Review Letters* **78(16)** (1997) 3201.
[28] A. Beznosov, E. Fertman, V. Desnenko, M. Kajňaková, A. Feher // *Journal of Magnetism and Magnetic Materials* **323(18-19)** (2011) 2380.