3B2v7.51c GML4.3.1 PHYSB : 23513 Prod.Type:com pp.1–3(col.fig.:NIL) ED:jss PAGN: keshava SCAN: archana

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Physica B ▮ (▮▮▮▮) ▮▮▮–▮▮▮

PHYSICA B

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Identification of first- and second-order magnetic phase transitions in ferromagnetic perovskites

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Abstract

A criterion used for the determination of first- and second-order magnetic phase transitions from purely magnetic methods is applied to manganese perovskites of formula $La_{2/3}(Ca_{1-x}Sr_x)_{1/3}MnO_3$. A crossover from first- to second-order character at a tolerance factor $t = 0.92$ is found, which also brings about several variations in other physical properties. At $t = 0.92$ a change from orthorhombic to rhombohedral symmetry also takes place. The impossibility of establishing static cooperative Jahn–Teller distortions in the rhombohedral symmetry is suggested as being responsible for the observed behaviour. © 2002 Published by Elsevier Science B.V.

Keywords: Manganites; Phase transitions; Jahn–Teller distortions

1. Introduction

The interpretation of the electric and magnetic properties of Ferromagnetic manganese perovskites of formula $A_{1-x}B_xMnO_3$ (A = rare-earth, B = divalent alkali) has been given traditionally on the basis of the double exchange (DE) mechanism. Nevertheless, after finding colossal magnetoresistance (CMR) close to the Curie temperature, T_C, of some of them [1,2], Millis et al. demonstrated that the DE picture is not enough to fit its magnitude quantitatively [3]. They proposed the addition, to the DE model, of a strong electron–phonon interaction arising from the Jahn–Teller (JT) splitting of the outer Mn d level. Later, de Teresa et al. found by small angle neutron scattering (SANS) magnetic polarons just above T_C [4], which can be considered as a form of phase segregation [5], and gave a new twist to the topic. More recently, both Uehara et al. [6] and Fäth et al. [7] have discovered that these materials are phase separated into a submicrometre-scale mixture of insulating regions and metallic ferromagnetic domains. The percolation of this inhomogeneous structure of coexisting metallic and more insulating areas would give the CMR effect and a change in the ordered ferromagnetic state. This idea, that had been previously invoked by Goodenough and Señarís Rodríguez for the understanding of parent ferromagnetic cobalt perovskites [8], was reproduced by the computational studies of models for manganese oxides of Moreo et al. [9]. These authors stress that coexisting clusters are induced by disorder on exchange and hopping amplitudes near first-order transitions of the nondisordered strongly coupled system. It is obvious then that it is a central issue to determine

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0921-4526/02/$ - see front matter © 2002 Published by Elsevier Science B.V.
PII: S0921-4526(02)00610-5

as to which samples present a first-order transition. Nevertheless, in spite of the clear academic definition of first- and second-order phase transitions, the experimental determination of such character is not always straighforward. We have revisited a criterion that allows the identification of the character of the transition by purely magnetic methods, and have applied it to a series of $A_{2/3}B_{1/3}MnO_3$ perovskites.

For the choice of samples we state that on the one hand, $La_{2/3}Ca_{1/3}MnO_3$ presents thermal hysteresis in resistivity [10] and other anomalies detected by neutron scattering [11], which indicate a first-order transition at T_C. On the other, $La_{2/3}Sr_{1/3}MnO_3$ seems to present a continuous ferromagnetic–paramagnetic phase transition [12,13]. We have then opted for a series of samples between these two extreme cases, and synthesized $La_{2/3}(Ca_{1-x}Sr_x)_{1/3}MnO_3$ with $x =$ 0, 0.05, 0.15, 0.25, 0.50, 0.75 and 1, in order to see where the crossover between both situations takes place. They were prepared by solid state reaction. See Ref. [14] for further details on preparation and characterization.

2. Results and discussion

The criterion used by us was proposed by Banerjee [15] on the basis of the theory of first-order transitions developed by Bean and Rodbell, who incorporated the molecular field model and exchange interaction that is strongly dependent upon lattice spacing [16]. With such an interaction, they calculated the minimum of the Gibbs free energy. Banerjee was the first to observe the essential similarity between the Bean–Rodbell approach and the classical formulation of Landau–Lifshitz [17]. He then concluded that a negative slope of isotherm plots of H/M vs. M^2 (M is the experimentally observed magnetization, H the magnetic field) would indicate a first-order phase transition. When applied to our series, we find that the change from first- to second-order takes place somewhere between 0.05 and 0.15 [14] (Fig. 1).

Now comes the following question: what is the reason for that? Samples between $x = 0.05$ and 0.15 correspond to a tolerance factor $t = 0.92$.

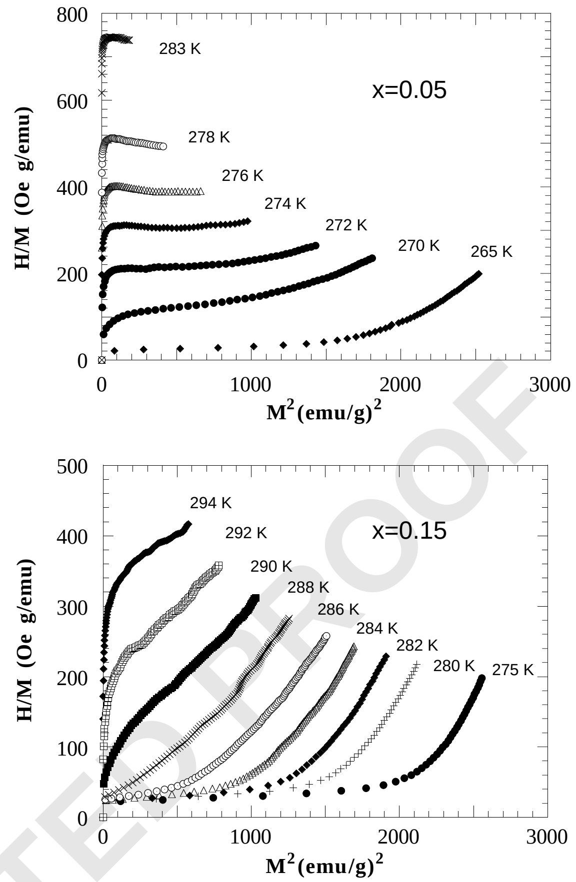

Fig. 1. H/M vs. M^2 plot of isotherms of the $x = 0.05$ and 0.15 samples. The slope turns from negative (first-order phase transition) to positive (second order).

Radaelli et al. find for a similar value of the tolerance factor a transition from rhombohedral to orthorhombic structure [18]. In the present case, the samples with $x = 0$ and 0.05 belong to the Pbnm space group, whereas for $x \geqslant 0.15$ the $R\bar{3}c$) space group is observed. It is a crucial variation: whereas static cooperative long-range Jahn–Teller distortions are possible in the Pbnm phase, the high symmetry of the MnO_6 octahedra in the $R\bar{3}c$) phase does not allow them [19,20] (the JT distortion modes are tetragonal or orthorhombic, rhombohedral symmetry does not split the e_g orbital).

It seems that the different role of the JT distortion underlies the alteration of the character of the transition at T_C. But this is not the only consequence. Dramatic variations of the physical properties between samples below and above $t = 0.92$ are also found. As examples we can mention that samples with $t < 0.92$ exhibit anomalous volume and magnetic entropy changes, high volume sensitivity to magnetic field and high MR, whereas those with $t > 0.92$ do not [21]. The list of changes across the value $t = 0.92$ is yet to be completed and experimental work is still lacking. Accordingly, we estimate the necessity to introduce a boundary line in the phase diagram of $A_{2/3}B_{1/3}MnO_3$ perovskites.

In the search for a reason, a possibility is that, for $t < 0.92$, the static cooperative JT deformations are replaced in the ferromagnetic phase by dynamic JT distortions which introduce vibrational modes into the spin–spin interaction [22,23]. A dynamic JT deformation gives isotropic ferromagnetic order between Mn ions by superexchange. Therefore, in $t < 0.92$ manganites superexchange would compete with the DE interaction.

This work is useful because after Moreo et al. [9], only manganites with first-order transitions will generate above T_C a structure of large coexisting metallic and insulating clusters with equal electronic density. As this seems to be a key condition for the production of CMR, we have found that, after the present work, manganites with $t < 0.92$ would be more favourable to observe larger CMR effects.

Acknowledgements

Spanish DGICYT MAT98-0416 is acknowledged for financial support.

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