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Magnetic behaviour near the magnetic-phase transition in $La_{1-x}Sr_xCoO_3$ ($0.20 \leqslant x \leqslant 0.30$) perovskites

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Abstract

Measurements of the temperature dependence of the magnetization (and parameters like coercivity and susceptibility) of $La_{1-x}Sr_xCoO_3$ ($0.20 \leqslant x \leqslant 0.30$) perovskites are presented. Particular attention is given to the interval of temperatures containing the ferro-paramagnetic phase transition. Curie temperature values lower than those reported previously and critical exponents are given. Additionally, the coercivity as well as the parameters of the law of approach to magnetic saturation are experimentally determined. Anomalies in Curie temperature, coercivity and law of approach to saturation are introduced confirming a non-conventional transition from ferromagnetic to paramagnetic states. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Perovskites; Phase transitions; Magnetic properties

Scientific research in $LaAMnO_3$ (A being alkaline earth) manganites is certainly one of the present hot topics in magnetism, owed to their large magnetoresistance ratios exhibited at the transition from ferromagnetic to paramagnetic [1]. On the other hand, $La_{1-x}Sr_xCoO_3$ cobaltates have also attracted much attention due to their interesting magnetic behaviour [2–4]. These cobaltates do not display a large magnetoresistance effect, although they present outstanding spin state transitions and perovskite-type structure which changes with temperature and substitution fraction x [2,5]. Substitution of divalent Sr for La gives rise to the appearance of tetravalent Co ions at the expense of trivalent ions so that, depending on the degree of substitution there is a mixture of low-spin and high-spin states. This doping would lead to the formation of island-like clusters and this results in a somehow anomalous magnetic behaviour. The presence of an interpenetrating metallic ferromagnetic phase within a non-magnetic phase has been proposed, being labelled as cluster-glass. With increasing temperature, the cluster-glass picture evolves towards a final paramagnetic phase at high enough temperatures. Because of their intrinsic non-homogeneous character, the peculiar magnetic behaviour of this series around the magnetic-phase transition is of fundamental interest. Accordingly, the aim of this work has been to investigate the temperature dependence of the magnetic properties for the $LaSrCoO_3$ series with particular emphasis in the temperature interval around that magnetic-phase transition.

Compounds of the family $La_{1-x}Sr_xCoO_3$ ($0.20 \leqslant x \leqslant 0.30$) with perovskite structure were prepared by conventional ceramic procedure and structurally characterised by X-ray diffraction. Magnetic properties were experimentally determined using both VSM and SQUID magnetometers in a temperature range between

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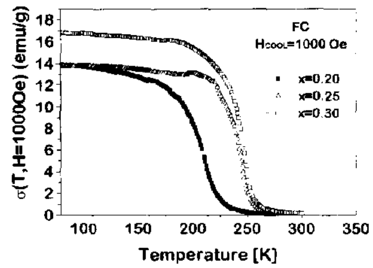

Fig. 1. Temperature dependence of the magnetic moment under a 10 Oe magnetic field for $La_{1-x}Sr_xCoO_3$ (1 kOe field cooled).

77 and 300 K and in fields up to $H = 5.5$ T. Fig. 1 shows the temperature dependence, measured under an applied field of 10 Oe, of the magnetization for several compounds after cooling down in a field of 1 kOe. A first rough evaluation of the Curie temperature, T_c, was performed using conventional kink point calculations through the minima of the dM/dT vs. T plots. Magnetization curves and hysteresis loops at different temperatures were measured and from them, characteristic parameters as the initial susceptibility, χ_o, and coercivity, H_c, were also evaluated.

In order to obtain precise values of the Curie temperature, T_c, and the critical exponents β and γ, modified Arrot plots and the Kouvel–Fisher method, with a self-consistent technique to obtain the best fitting, have been analysed [6]. These critical parameters are defined by the exponential laws

$$M_s(T) \approx (T_c - T)^\beta \quad \text{for } T_c > T\,,$$

and

$$(\chi_o)^{-1}T \approx (T - T_c)^\gamma \quad \text{for} \quad T_c < T. \tag{1}$$

The values for T_c obtained are 198.5 (210), 222.3 (247) and 223.4 (246) K for $x = 0.20$, 0.25 and 0.30, respectively (values deduced from the kink point calculations are given in parenthesis). It must be noticed that there is a considerable difference in the values obtained by each method. In fact, our previously reported values for T_c appear closer to those given in parenthesis [2,4]. The critical exponents, β and γ, had values of 0.46 and 1.38, respectively. It should be emphasized that there is a lack of previous results concerning the critical exponents of this perovskites series, as well as an important spread of the values reported for other similar structures. The values of the Curie points and critical exponents are analysed in deeper detail elsewhere [7].

To obtain information on the high-field behaviour near the critical region, magnetization curves were measured using fields as high as 5.5 T. The law of approach to

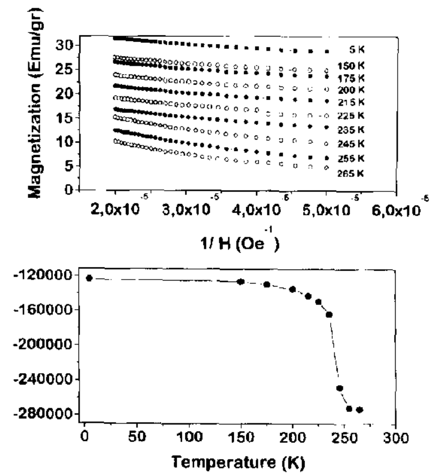

Fig. 2. High-field behaviour of magnetization as a function of the inverse applied field (a) and the a_1 coefficient of the law of approach to saturation for $x = 0.30$ (b).

magnetic saturation has been analysed considering the general expression:

$$M/M_s = \Sigma_i(a_i/H^i) + bH^{1/2}, \tag{2}$$

where a_i denote the coefficients for the corresponding H^i terms. Fig. 2a shows the magnetization of the sample with $x = 0.3$ as a function of the inverse applied field for different temperatures. As a general comment, we can say that these coefficients take rather high values which indicate a somehow strong difficulty to reach saturation as a consequence of the cluster-glass nature of the sample. Fig. 2b shows the temperature dependence of the a_1 coefficient, which exhibits a clear increase below the Curie temperature. Still measurable values are obtained in the interval of temperatures just above the evaluated order temperature, indicating that some type of magnetic structures are still present.

Finally, the temperature dependence of coercivity was measured. Fig. 3 shows the result for the sample with $x = 0.30$. As in the previous set of measurements, anomalies around the order temperature are observed since coercivity shows non-negligible values just above the Curie point. Moreover, the correlation between temperature dependence of coercivity, H_c, and that of spontaneous magnetization, M_s, as derived from the modified Arrot plots has been checked considering $H_c(T) \propto M_s(T)^n$. A value of $n \approx 4.1$ is found (see inset of Fig. 3) which in principle is associated to a relatively five-fold basal magnetic anisotropy that should be correlated to the structure nature of the perovskite.

An anomalous magnetic character has been found in the region around the Curie temperature, in particular for the sample with substitutional degree $x = 0.30$. It is

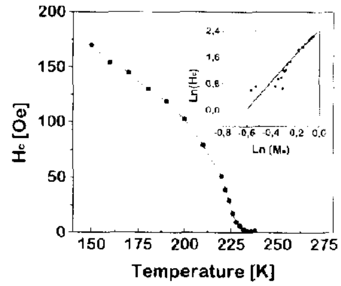

Fig. 3. Temperature dependence of coercivity for $x = 0.30$. Inset shows the correlation between the temperature dependences of coercivity and saturation magnetization.

firstly remarkable that there is a difference in the value of the order temperature when magnetic measurements are analysed by different methods (kink point and Arrot plots). In fact a variation of more than 20 K is observed. This peculiar character is also deduced from the non-vanishing values of the coercivity and the coefficients of the law of approach to saturation. Recent reports on this series also support this anomalous behaviour around the Curie temperature. Magnetostriction takes vanishing values not before 250 K [8], while neutron and small angle scattering experiments reveal the existence of regions of short-range ferromagnetic order above T_c [9]. Finally, it might be of interest to mention that these samples, metallic in all the analysed temperature range, show a change of the slope of resistivity at the magnetic order transition due to magnon scattering, analogously to the observed in parent manganites. In short, we can conclude the magnetic transition from non-homogeneous cluster-glass ferromagnetism to paramagnetic behaviour takes place seemingly, not in a sharp conventional way, since the temperature interval for the transition is rather extended.

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