EUROPHYSICS LETTERS

OFFPRINT

Vol. 62 • Number 3 • pp. 433–438

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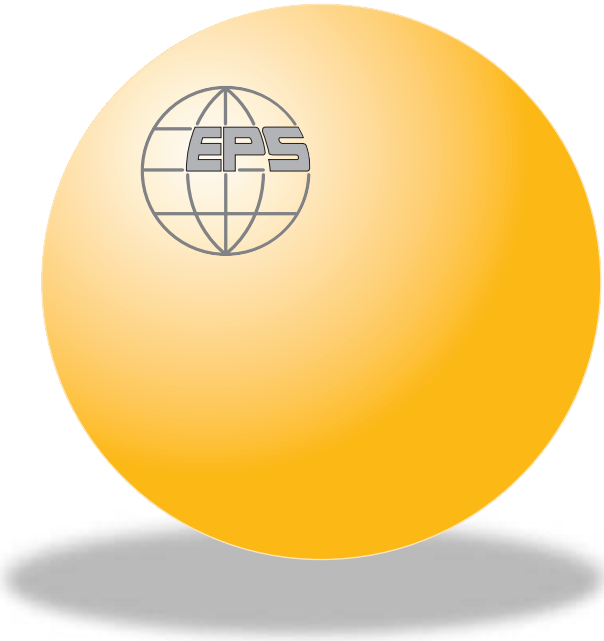

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EUROPEAN PHYSICAL SOCIETY
Incorporating
JOURNAL DE PHYSIQUE LETTRES • LETTERE AL NUOVO CIMENTO

EUROPHYSICS LETTERS 1 May 2003

Europhys. Lett., **62** (3), pp. 433–438 (2003)

Field-induced magnetic anisotropy in $La_{0.7}Sr_{0.3}CoO_3$

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(received 20 September 2002; accepted in final form 7 March 2003)

PACS. 75.30.Gw – Magnetic anisotropy.
PACS. 75.30.Cr – Saturation moments and magnetic susceptibilities.
PACS. 71.70.Ej – Spin-orbit coupling, Zeeman and Stark splitting, Jahn-Teller effect.

Abstract. – Magnetic anisotropy has been measured for the ferromagnetic $La_{0.7}Sr_{0.3}CoO_3$ perovskite from an analysis of the high-field part of the magnetization *vs.* field curves, *i.e.*, the magnetic saturation regime. These measurements give a magnetic anistropy one order of magnitude higher than that of reference manganites. Surprisingly, the values of the magnetic anisotropy calculated in this way do not coincide with those estimated from measurements of coercive fields which are one order of magnitude smaller. It is proposed that the reason of this anomalous behaviour is a transition of the trivalent Co ions under the external magnetic field from a low-spin to an intermediate-spin state. Such a transition converts the Co^{3+} ions into Jahn-Teller ions having an only partially quenched orbital angular momentum, which enhances the intra-atomic spin-orbit coupling and magnetic anisotropy.

Attention to cobalt perovskites of formula $R_{1-x}A_xCoO_3$ was first paid in the '50s. At that time, Jonker and van Santen [1] and Koehler and Wollan [2] described their basic properties, that were first interpreted by Goodenough [3]. The finding of colossal magnetoresistance effects in Mn perovskites [4,5] reactivated the interest on these and related materials, like the title compound. Since the first investigations, it was seen that the magnetic and transport properties of cobalt perovskites have a peculiar thermal dependence [2, 6–10]. To explain it, the existence of a thermally induced change in the electronic configuration of the Co ions was established by Raccah and Goodenough [7]. It is a consequence of the interplay between the intra-atomic exchange and the crystal electric-field interactions, which in this particular compound are of comparable magnitude. This fact is highlighted as the source of many of

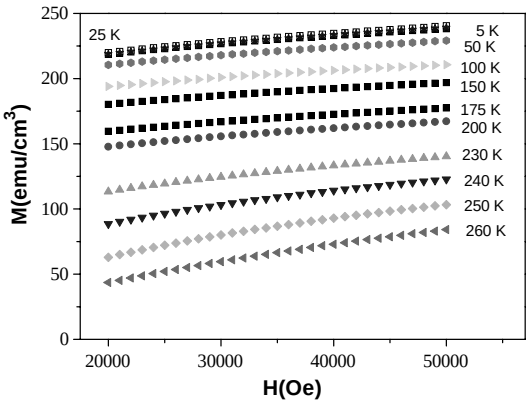

Fig. 1 – Magnetization *vs.* magnetic field in the saturation regime of $La_{0.7}Sr_{0.3}CoO_3$. In fields up to 55 kOe the material is still far from saturation, indicating a strong magnetic anisotropy.

the differences with manganites [11], where the intra-atomic exchange is rather higher than the crystal electric-field interaction. For the particular case of $LaCoO_3$, the electronic state changes at intermediate temperatures. At low temperatures, the predominant state is low-spin (t_{2g}^6, $S = 0$) and, at intermediate ones, it evolves to an intermediate- ($t_{2g}^5 e_g^1$, $S = 1$) or high-spin state ($t_{2g}^4 e_g^2$, $S = 2$) [7,8,10,12–18], due to the small energy gap ($\simeq 0.03$ eV) between such configurations. Sr-doping leads to a phase segregation into hole-rich ferromagnetic clusters and a hole-poor $LaCoO_3$-like matrix [19,20]. The hole-rich regions are isolated for low x, but at $x \simeq 0.20$ they percolate and the samples become ferromagnetic and metallic. The phase diagram of this very complex system has been given by Señarís Rodríguez and Goodenough [19].

One of the specific features of $La_{0.7}Sr_{0.3}CoO_3$ is the difficulty of approaching a magnetic saturation state [11,19,21,22]. This has been attributed to the absence of true long-range order, that leads to a cluster-glass state [21]. Nevertheless, the ultimate origin of the situation is still not clear, and some hypotheses have been launched recently, like the presence of diamagnetic $S = 0$ Co ions that would dilute the magnetic lattice [11]. In any case, after the percolation of the hole-rich ferromagnetic clusters the system can be considered as a ferromagnet.

As a new input to this puzzle, Ibarra *et al.* reported recently a huge anisotropic magnetostriction [23] that cannot be explained on the basis of the usual spin-orbit coupling contribution. To explain it, they proposed an orbital instability of Co^{3+} under an external magnetic field. In this work the hypothesis of the orbital instability is adopted to analyze the high magnetic anisotropy of the $La_{0.7}Sr_{0.3}CoO_3$ system.

The sample was prepared by conventional ceramic methods. X-ray powder diffraction revealed that it was single phase. Initial magnetization data were taken with vibrating-sample and SQUID magnetometers in fields up to 55 kOe. Before each run, the sample was demagnetized heating up to 350 K, well above the Curie point, and cooled down to the test temperature at zero field.

In fig. 1 the high-field part of the magnetization *vs.* magnetic-field isotherms is shown. As can be seen, the difficulty to achieve saturation is greater than in ferromagnetic manganites. In order to analyze the approach to saturation magnetization, we use the empirical relationship [24, 25]

$$M_H = M_S(T) - \frac{a}{H} - \frac{b}{H^2} + \chi H, \tag{1}$$

where M_H is the component of the magnetization along the field direction, M_S is the saturation

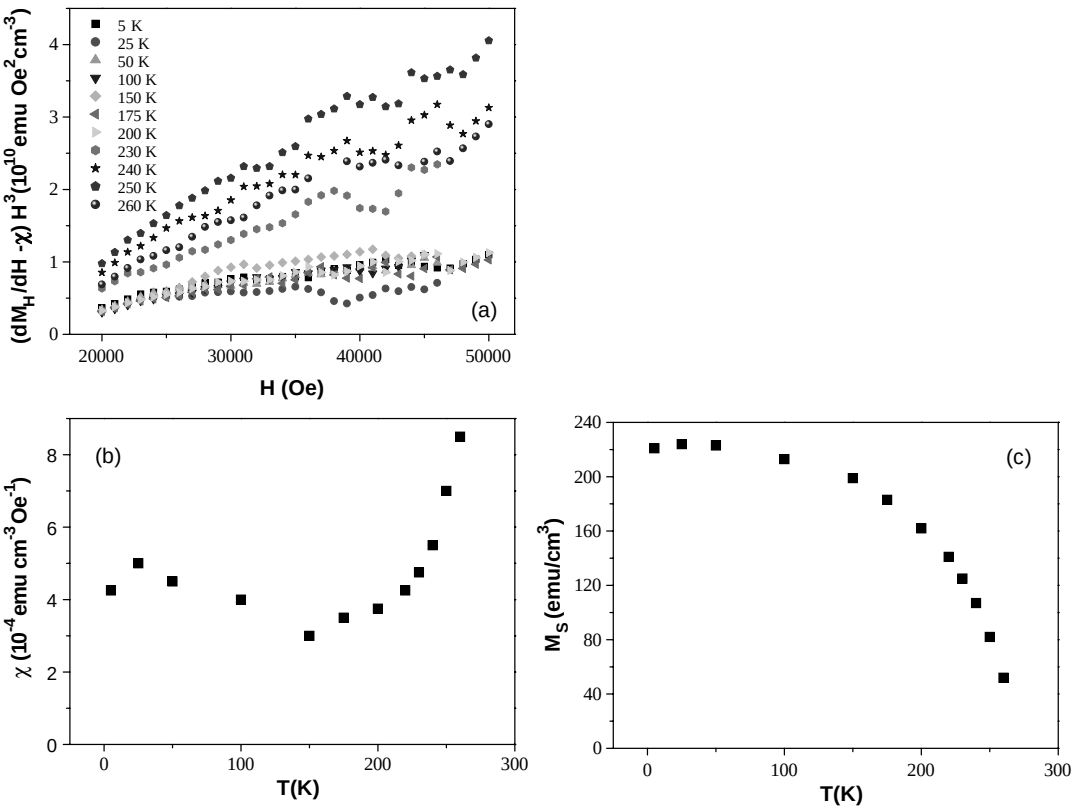

Fig. 2 – (a) Representation of the magnetization *vs.* field isotherms of $La_{0.7}Sr_{0.3}CoO_3$ according to eq. (2). (b) Values of χ used for the representations of (a). (c) Saturation magnetization obtained from the fits of the isotherms to eq. (1).

magnetization and a, b and χ are constants. The term χH represents the field-induced increase in the spontaneous magnetization of the domains and it is very small at temperatures well below the Curie temperature. The a/H term is generally interpreted as due to imperfections such as dislocations or nonmagnetic inclusions, and b/H^2 is due to crystalline anisotropy. To expedite the fits, the derivative is often used [24]

$$\left(\frac{\mathrm{d}M_H}{\mathrm{d}H} - \chi\right) H^3 = aH + 2b. \tag{2}$$

Data were fitted to achieve the χ that best linearizes the curves. In fig. 2(a) we show the representation of the magnetization according to eq. (2), with the χ's shown in fig. 2(b). Linear fits were then done for data above 30 kOe in order to obtain a and b. These data, substituted in eq. (1), allow to fit the magnetization data and to determine the saturation magnetization shown in fig. 2(c).

From the value of b, the values of the anisotropy constant can be calculated. For a polycrystalline material with crystallites oriented at random, the approach to saturation may be calculated by averaging the magnetization curves for all crystal orientations [26]. The b

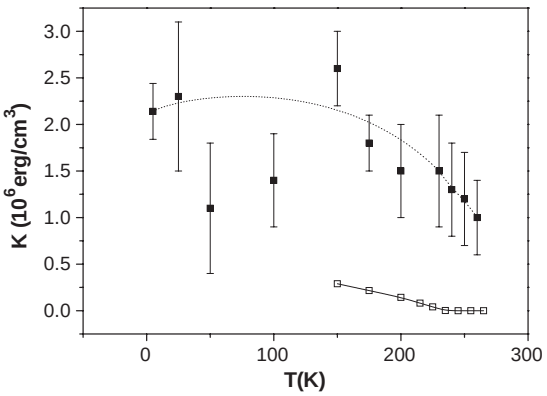

Fig. 3 – Magnetic anisotropy *vs.* temperature for $La_{0.7}Sr_{0.3}CoO_3$, extracted from fits of the high-field linear part of magnetization *vs.* field curves (filled symbols) as well as from data of coercive fields (open symbols).

constant is then given by [27]

$$b = \beta \frac{K^2}{M_S}\,, \tag{3}$$

where β comes from purely geometric considerations. As this study only estimates the orders of magnitude of the magnetic anisotropy, we chose the same value of $\beta = 8/105$ used for the reference manganese perovskite $La_{2/3}Sr_{1/3}MnO_3$ (ref. [28]), understanding that the choice does not affect the final results. The values thus obtained for the anisotropy constant are reported in fig. 3.

The effects of magnetocrystalline anisotropy are detectable in other features of ferromagnetic materials, like the value of coercive fields. The coercive field can be estimated from the results of fig. 2 with the well-known relation

$$H_{\mathrm{C}}(T) = A \frac{K}{M_0(T)}\,, \tag{4}$$

where A is a constant typically between 0.1 and 1 (ref. [29]) and M_0 is the spontaneous magnetization. Taking into account that for $T < 0.8 T_{\mathrm{C}} M_0 \simeq M_S$ (M_S can be used instead of M_0 at low temperatures), we arrive at the fact that expected coercive fields are of the order of 10^3 or 10^4 Oe. The coercive fields of $La_{0.7}Sr_{0.3}CoO_3$ have already been reported by Vázquez *et al.* [22]; surprisingly, a clear discrepancy is found with the values expected from eq. (4), in one or two orders of magnitude, depending on the A value.

A deeper insight is needed, and the value of A is important to quantify this anomaly. In order to determine A, we have analyzed the manganite $La_{0.7}Ca_{0.3}MnO_3$. From magnetization *vs.* field isotherms at 5 K and fitting the high-field part in the same way as previously, we obtain $K = 3.4 \cdot 10^5\,\mathrm{erg/cm^3}$ ($5.86 \cdot 10^4\,\mathrm{erg/g}$), which is consistent with the results of Perekalina *et al.* [30], who give values ranging from $3.5 \cdot 10^4$ to $6 \cdot 10^4\,\mathrm{erg/g}$ for the magnetic anisotropy of $La_{0.7}(Sr, Pb)_{0.3}MnO_3$. It is worth mentioning that this value is one order of magnitude smaller than that of the cobaltite. Provided that coercive fields at 5 K are of the order of ~ 50 Oe and $M_S \sim 650\,\mathrm{emu/cm^3}$, we arrive at the conclusion that $A \simeq 0.1$, which will be used for the analysis of $La_{0.7}Sr_{0.3}CoO_3$. With this value of A and the data of H_{C} and M_S, we can recalculate the anisotropy constant by eq. (4). The result is shown in fig. 3. A simple comparison of these data (measured from coercive fields, *i.e.*, at low applied magnetic fields)

with fig. 3 (obtained from the high-field regime) show that they are around one order of magnitude smaller.

The question now is to identify what is happening with the magnetic anisotropy of this compound. For the measurements of the two sets of anisotropy constant values (expected in principle to be similar), the only external parameter that has been changed is the external magnetic field. In one case it is high (saturation regime) and in the other it is low (when measuring coercive fields, that are of the order of 10^2 Oe). Then, it seems that the magnetic anisotropy constant of $La_{0.7}Sr_{0.3}CoO_3$ does not remain the same under external magnetic fields. We see a strong parallelism of this situation with the finding by Ibarra *et al.* [23] of a huge anisotropic magnetostriction induced by the external magnetic field. They concluded that the anisotropic magnetostriction cannot be explained on the basis of the usual spin-orbit contribution and proposed that it is due to the orbital instability of the Co ions under the external applied field, *i.e.*, on the transformation of the low-spin state of the Co^{3+} ions in the insulating matrix (which is diamagnetic and does not contribute to magnetic anisotropy) into the energetically close intermediate-spin configuration, which is a Jahn-Teller ion. As described by Ibarra *et al.* [23], under Jahn-Teller distortion, the doubly degenerated e_g level of IS-Co^{3+} splits into two singlets ($L = 0$), and the triplet t_{2g} into a singlet and a doublet ($L = 1$). The singlet states of the t_{2g} level are occupied by two electrons with opposite spins and the doublet level by three electrons. Due to the degeneracy of the doublet level with nonzero angular momentum, a strong intra-atomic spin-orbit coupling is created which leads to the increase in magnetic anistropy, in contrast to the reference manganese perovskites. Our result can also be interpreted as another evidence in favour of the orbital instability of the Co ions under external magnetic fields in $La_{0.7}Sr_{0.3}CoO_3$.

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Spanish MCYT, under project FEDER MAT2001-3749, is acknowledged. We also wish to thank L. E. Hueso for data on $La_{0.7}Ca_{0.3}MnO_3$.

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