Effects of Sr doping on the magnetic properties of Sr$_x$Ba$_{1-x}$CoO$_3$

V. Pardo, J. Rivas, and D. Baldomir

$^1$ Departamento de Física Aplicada, Facultad de Física, Universidad de Santiago de Compostela, E-15782 Campus Sur s/n, Santiago de Compostela, Spain

$^2$ Instituto de Investigaciones Tecnológicas, Universidad de Santiago de Compostela, E-15782, Santiago de Compostela, Spain

Magnetic properties of the Sr-doped BaCoO$_3$ are explained on the basis of ab initio calculations and the analysis of experimental literature. Formation of magnetic clusters bigger than in the parent compound and increase in the blocking temperature are observed. Superparamagnetism remains at room temperature. The possibility of tuning the size and properties of the magnetic clusters with doping is explored.

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Ab initio electronic structure calculations are becoming increasingly important in materials science. The improvement of the codes and the ever increasing capabilities of modern supercomputers has produced a comparable improvement in the precision of the properties of solids which are attainable nowadays by means of, e.g., density functional theory calculations. The connection with the real physical properties of the materials is already possible and the project of designing materials theoretically has been under way for the last few years.

Transition metal oxides have drawn the attention of the scientific community for the last 50 years because of their interesting physical properties and multiple applications. Co oxides are becoming increasingly important, mainly because of their thermoelectric, magnetoresistive, and superconducting properties. These materials also present difficulties for the ab initio calculations because of having strongly correlated electrons; the use of the LDA+U method or dynamical mean field theory is needed to predict their properties correctly.

Systems formed by magnetic nanostructures have been studied intensively in the last few years, showing some interesting technological applications, in fields such as magnetic recording, sensors, MRAM and magnetoelectronics. E.g., Co nanocrystals have also numerous applications due to their special magnetic properties.

In a recent paper, the magnetic properties of BaCoO$_3$, were analyzed considering the formation of nanometric magnetic clusters, ferromagnetic regions embedded in a non-ferromagnetic matrix, in the material, starting from experimental data and interpreting them by means of ab initio calculations. Glassy behavior has also been recently found in similar compounds. This is usually related to having a sort of self-generated assembly of magnetic clusters in which magnetic interactions introduce glassiness among them or a competition between ferromagnetic and antiferromagnetic couplings which may lead to frustration of any long range magnetic order, as it is the case in BaCoO$_3$.

In this paper, we will discuss how these magnetic clusters change with Sr-doping, focusing in the half-doped compound Sr$_0.5$Ba$_0.5$CoO$_3$. The description of its magnetic properties will be made using the experimental data available, interpreted via ab initio calculations.

The temperature and applied field dependence of the magnetization measured after cooling in zero field (ZFC) and after cooling in a field (FC) in Ref. Fig. 12 suggest us that the Sr-half-doped compound behaves as an assembly of non-strongly interacting particles, which we proceed to analyze. Two cusps appear in the ZFC magnetization curves, one at 50 K and another one at about 140 K, being the cusp at about 50 K a remainder of the parent compound which comes out in the doped case because of the fabrication procedure. The physics which is genuine of the doped compound is shown by the higher temperature one. This so-called bimodality, i.e., the appearance of two types of magnetic particles of different sizes in one sample, is usually found in granular systems. Similar curves could also be understood taking into account the effects of the surface of the clusters but we have ruled this possibility out because of the technique used to produce the sample, which would tend to conserve a matrix with the properties of the parent compound.

For describing properly what the magnetic morphology of the system is we need to characterize the size of these magnetic clusters and the interparticle distance. For doing so, we will make use of ab initio calculations performed with the WIEN2k software, which uses an APW+lo full-potential method and the LDA+U approach in the “fully-localized limit” to deal with the strong correlations typically present in transition metal oxides.

The blocking temperature of Sr$_0.5$Ba$_0.5$CoO$_3$ is, as can be seen in Ref. Fig. 12, at about 140 K. With this value, the size of the magnetic clusters which become blocked below that temperature, but act as superparamagnetic particles above it (see Fig. 1), can be estimated with the knowledge of the anisotropy constant of the material. This quantity can be calculated ab initio just by computing the total energy of the material, including spin-orbit effects in a second variational manner, assuming the magnetic moments lie in the different crystallographic directions. We calculated the anisotropy constant...
constant as $K = \frac{E_B}{V}$ (we assume cubic anisotropy due to the nearly octahedral environment where the Co ions are), where the magnetocrystalline energy $E_B$ is defined as the work required to make the magnetization lie along the hard $(a)$ axis compared to an easy $(c)$ direction. We must note here that the introduction of Sr produces severe changes in the crystalline anisotropy energy of the material. It changes the easy axis from the hexagonal plane where it lies in the parent compound to the Co-chains axis $(c)$. Also, the magnitude of the anisotropy constant has in the doped compound a value of $1.5 \times 10^5 \text{erg/cm}^3$, which is one order of magnitude smaller than in the parent compound, but still larger than the typical values for systems of Co magnetic particles, hence, still one can assume that the formation of the clusters will have a much smaller contribution to the magnetic anisotropy of the system and consider that the magnetocrystalline anisotropy is the dominant effect.

The size of the clusters can then be obtained using the well-known expression for systems of superparamagnetic particles\textsuperscript{31}: $KV = 25k_BT_B$, where $K$ is the anisotropy constant, $V$ is the typical volume of the particles, $T_B$ is the blocking temperature (which is about 140 K in this case), $k_B$ is the Boltzmann’s constant and the factor 25 appears due to the experimental technique. The typical volume of the clusters which comes out of our calculations is about 4 nm in diameter, comprising some 500 Co atoms. The size of these clusters is much bigger than those forming the parent compound, which are about 1.2 nm in diameter\textsuperscript{22}, but these are still present in the doped sample utilized in Ref. 22 accompanied of the bigger ones due to the half-doped material. These determine the magnetic properties of the compound above some 100 K and also at room temperature, where superparamagnetism remains for the case of the Sr-doped compound, whereas in the parent compound, the breaking of the clusters occurs at about 250 K and paramagnetism is the phase at room temperature\textsuperscript{22}. Below 100 K, the properties are determined by the remaining of the smaller clusters, which become blocked below approximately 50 K. In the half-doped compound, magnetic clusters containing about 500 Co atoms exist at room temperature. The possibility of controlling the size and properties of the magnetic particles with doping is clear. Introducing Sr into the undoped BaCoO$_3$ produces the appearance of bigger clusters which can be observed already for the compound Sr$_{0.2}$Ba$_{0.8}$CoO$_3$ (see in Ref. 22, Fig. 11 how a second cusp starts to develop in the ZFC curve at a higher temperature). The control of the size and magnetic properties of the clusters can also be done by changing the magnetic field\textsuperscript{22}, but here we propose a different way to do so, i.e., doping the sample with an isovalent cation. Moreover, here we are dealing with magnetic particles which spontaneously occur in the system and whose properties can be tuned by changing the dopant concentration.

The formation of magnetic clusters in the series Sr$_x$Ba$_{1-x}$CoO$_3$ ($x \leq 0.5$) is probably related to the degeneracy of both ferromagnetic and antiferromagnetic configurations\textsuperscript{32}. Our calculations on the half-doped compound yield a similar behavior to that found in the parent compound\textsuperscript{22}, ferromagnetism is marginally more stable but it is orbital ordering the main energetic contribution, so-called alternating orbital ordering along the Co chains\textsuperscript{21} is about 50 meV/Co more stable than the “ferro-orbital” solution, whereas energy differences due to magnetic ordering are one order of magnitude smaller. The interplay between double exchange favoring ferromagnetism and superexchange favoring antiferromagnetism might produce frustration in this type of compounds and a cluster-glass behavior could turn out as a result. However, this does not seem the case from the susceptibility curves we can see in Ref. 22, which do not show strong interactions between the clusters.

In Fig. 1 we plot the data of magnetization vs. H/T which appears in Ref. 22 (inset of Fig. 12) as several curves of magnetization vs. magnetic field for different temperatures. The curves superpose as expected for a system of superparamagnetic particles above the blocking temperature. As mentioned above, superposition is maintained for the curve at 400 K, indicating that, at room temperature and above, magnetic clusters still exist and determine the magnetic properties of the material. At high temperatures, the slope grows because the clusters get bigger (a lower anisotropy constant when temperature increases implies higher volume of the clusters).

These curves can be fit to a Langevin formula, which approximates to a Curie law at small values of the ratio $\frac{H}{k_BT}$, where $\mu$ is the magnetic moment of the cluster, in the following way: $M \simeq N \frac{\mu^2 H}{3k_BT}$, where $N$ is the density of clusters in the material. From this fitting of the curves in Fig. 1 one can estimate the density of clusters $N$, which determines the way these clusters interact.
and also the shape of the FC curve below the blocking temperature. The result is that there is one cluster formed by about 500 Co atoms in a spherical volume with a diameter of approximately 8 nm. Hence, the average distance between clusters is about 2 diameters. This means that the clusters do not strongly interact with each other, as it becomes clear from Ref. 22, Fig. 12, where it can be observed that the FC curve below 140 K (the blocking temperature) rises as expected for non-strongly-interacting particles, even though this shape might depend on the cooling speed. Cluster-glass behavior is not observed in the sample and this is confirmed by the calculations showing that the clusters are not strongly interacting (they are far enough from each other).

In this paper we have presented an explanation for the magnetic properties of the series Sr$_x$Ba$_{1-x}$CoO$_3$ characterized by means of ab initio calculations. The presence of the clusters is an essential ingredient in the description of the magnetic properties of the material. When Ba is substituted by Sr, the magnetic clusters increase in size and superparamagnetism remains at room temperature for the half-doped compound. The possibility of tuning the magnetic properties of a system of superparamagnetic clusters by doping with an isovalent cation is explored. It would be interesting to analyze what happens to the system when doping it with a different divalent cation such as Ca. The reasoning we follow in this letter might be extended to other similar compounds showing phase segregation, which are of key importance for nanoscience and nanotechnology. We state the possibility of studying these variations in magnetic properties by means of electronic structure ab initio calculations.

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1. P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).
2. P. Baettig and N. Spaldin, Appl. Phys. Lett. 86, 012505 (2005).
3. Y. Tokura, Colossal magnetoresistive oxides (Australia: Gordon and Breach Science Publishers, 2000).
4. I. Terasaki, Y. Sasago, and K. Uchinokura, Phys. Rev. B 56, R12685 (1997).
5. C. Martin, A. Maignan, D. Pelloquin, N. Nguyen, and B. Raveau, Appl. Phys. Lett. 71, 1421 (1997).
6. K. Takada, H. Sakurai, E. Takayama-Muromachi, F. Izumi, R.A. Dilanian, and T. Sasaki, Nature (London) 422, 53 (2003).
7. V.I. Anisimov, F. Aryasetiawan, and A.I. Lichtenstein, J. Phys.: Condens. Matter 9, 767 (1997).
8. V.I. Anisimov, A.I. Poteryaev, M.A. Korotin, A.O. Anokhin, and G. Kotliar, J. Phys.: Condens. Matter 9, 7359 (1997).
9. E.P. Wohlfarth, J. Phys: F Metal Phys. 10, L241 (1980).
10. J.I. Martín, J. Nógués, K. Liu, J.L. Vicent, and I.K. Schuller, J. Magn. Magn. Mater. 256, 449 (2003).
11. Y. Gao, Y. Bao, M. Beerman, A. Yasuhara, D. Shindo, and K.M. Krishnan, Appl. Phys. Lett. 84, 3361 (2004).
12. V. Pardo, J. Rivas, D. Baldomir, M. Iglesias, P. Blaha, K. Schwarz, and J.E. Arias, Phys. Rev. B 70, 212404 (2004).
13. M.A. Señarís Rodríguez, and J.B. Goodenough, J. Solid State Chem. 118, 323 (1995).
14. J. Mira, J. Rivas, R.D. Sánchez, M.A. Señarís Rodríguez, D. Fiorani, D. Rinaldi, and R. Caciuffo, J. Appl. Phys. 81, 5753 (1997).
15. J. Mira, J. Rivas, K. Jonason, P. Nordblad, M.P. Breijo, and M.A. Señarís Rodríguez, J. Magn. Mag. Mater. 196-197, 487 (1999).
16. J. Mira, J. Rivas, G. Baio, G. Barucca, R. Caciuffo, D. Rinaldi, D. Fiorani, and M.A. Señarís Rodríguez, J. Appl. Phys. 89, 5606 (2001).
17. H. Szymczak, M. Baran, G.J. Babonas, R. Diduszk6, J. Fink-Finowicki, and R. Szymczak, J. Magn. Magn. Mater. 285, 386 (2005).
18. J. Rivas, J. Mira, D. Rinaldi, R. Caciuffo, and M.A. Señarís Rodríguez, J. Magn. Magn. Mater. in press (2005).
19. F. Rivadulla, M.A. López-Quintela, and J. Rivas, Phys. Rev. Lett. 93, 167206 (2004).
20. J. Rivas, F. Rivadulla, and M.A. López-Quintela, Phys. B. 354, 1 (2004).
21. V. Pardo, P. Blaha, M. Iglesias, K. Schwarz, D. Baldomir, and J.E. Arias, Phys. Rev. B 70, 144422 (2004).
22. K. Yamaura, H.W. Zandbergen, K. Abe, and R.J. Cava, J. Solid State Chem. 146, 96 (1999).
23. M. Blanco-Mantecón and K. O’Grady, J. Magn. Magn. Mater. 203, 50 (1999).
24. E. De Biasi, C.A. Ramos, R.D. Zysler, and H. Romero, Phys. Rev. B 65, 144416 (2002).
25. E. Tronc, D. Fiorani, M. Nógués, A.M. Testa, F. Lucari, et al., J. Magn. Magn. Mater. 262, 6 (2003).
26. K. Schwarz and P. Blaha, Comp. Mat. Sci. 28, 259 (2003).
27. E. Sjöstedt, L. Nördstrom, and D.J. Singh, Solid State Commun. 114, 15 (2000).
28. A.I. Lichtenstein, V.I. Anisimov, and J. Zaanen, Phys. Rev. B 52, R5467 (1995).
29. A.G. Petukhov, I.I. Mazin, L. Chioncel, and A.I. Lichtenstein, Phys. Rev. Lett. 87, 153106 (2002).
30. D.J. Singh, Planewaves, pseudopotentials and LAPW method (Kluwer Academic Publishers, 1994).
31. A.H. Morrish, The Physical Principles of Magnetism (IEEE Press, New York, 2001).
32. K. Binder and A.P. Young, Rev. Mod. Phys. 58, 801 (1986).
33. J.L. Dormann, D. Fiorani, and E. Tronc, Adv. Chem. Phys. 98, 283 (1997).
34. J. García-Otero, M. Porto, J. Rivas, and A. Bunde, Phys. Rev. Lett. 84, 167 (2000).