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Antisite defects and magnetoresistance in Sr_2FeMoO_6 double perovskite

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Abstract

We report a detailed study of the magnetic and magnetotransport properties of Sr_2FeMoO_6 ceramics having a controlled concentration of antisite (AS) defects. It is found that a high-field differential susceptibility exists in all samples, which increases with AS. Similarly, a high-field magnetoresistivity develops and mimics the differential susceptibility. These observations suggest that antisite defects promote some magnetic frustration. High-resolution electron microscopy studies have allowed observation of the existence of antiphase boundary defects in the Sr_2FeMoO_6 structure.

1. Introduction

Double perovskite oxides of the type $A_2MM'O_6$ are receiving a great deal of attention because their half-metallic ferromagnetism leads to promising expectations for spin devices [1]. Indeed, their Curie temperature T_C can be as high as 415 K in Sr_2FeMoO_6 [1], well above the optimal $T_C \approx 360$ K of the celebrated $La_{2/3}Sr_{1/3}MnO_3$ manganite. The structural building blocks ABO_3 of these double perovskites are ordered in a three-dimensional network, in such a way that the B sites of the perovskite unit are alternatively occupied by M and M′ ions. The magnetic structure was early described as ferrimagnetic due to an antiferromagnetic coupling of B and B′ sublattices [2]. For instance, in Sr_2FeMoO_6 parallel alignment of $Fe^{3+}(d^5; S = 5/2)$ spins in the B sublattice, antiferromagnetically coupled to $Mo^{5+}(d^1; S = 1/2)$ spin leads to an expected saturated moment of $M_S = 4\mu_B$. Remarkably enough, the measured values of M_S in these oxides are systematically lower than the predicted value; it is commonly though that this effect could be related to antisite defects in the B/B′ sublattices, i.e. occupation of Fe(Mo) ions in the Mo(Fe) sites [1, 3]. Recently, a systematic study of the Mo/Fe ordering and its correlation

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with the saturation magnetization has indeed proved that antisite (AS) defects are the primary cause of a reduced magnetization [4].

Much in common with the manganites, these materials display a substantial magnetoresistance at T_C, related to the suppression of spin fluctuations at the Curie temperature [5]. Ceramic samples also display a significant low-field magnetoresistance (MR) that is believed to be related to intergranular spin tunnelling and which extends and grows to the lowest temperatures [1, 6]. In spite of the intense research on these materials, particularly on Sr_2FeMoO_6, there are still a number of issues that have not been appropriately addressed so far. One of the most striking observations is the weak magnetoresistance observed across artificial grain boundaries in epitaxial thin films grown on bicrystalline substrates [7], which sharply contrasts with results obtained in manganite films [8]. This remarkable difference has been attributed to the existence of antiphase boundaries defects [9] although evidence has not been provided so far.

In this paper, we will explore the high-field magnetization process and the corresponding magnetoresistance of samples having a controlled density of AS defects. We will show that there is a close connection between the AS defect concentration AS and the difficulty to magnetically saturate the material. This behaviour could be easily understood if AS defects were the source of a significant magnetic frustration. However, this should not be expected if the ferrimagnetic ordering in these oxides were of superexchange origin. This observation would deny the superexchange ferrimagnetic model and is consistent with a double-exchange-like mechanism. This conclusion is in agreement with recent results that have shown that the dominant interaction is ferromagnetic but not antiferromagnetic as expected in a ferrimagnetic ordering [10]. On the other hand, antiphase boundaries (APBs) are a rather common extended defect in structures formed by ordering of distinct structural units as observed in magnetite and even in high-temperature superconducting cuprates. In the present case, the building blocks are the $SrFeO_3$ and $SrMoO_3$ and APBs are formed when Fe(Mo)–O planes are substituted by Mo(Fe)–O planes; the APBs formed may behave as a strongly pinned domain wall and thus may produce a substantial high-field differential susceptibility [9]. From high-resolution electron microscopy (HREM) images, we have been able to observe, for the first time, APB defects in some samples; however, no correlation could be established between their occurrence and the χ_d. On the other hand, the high-field magnetoresistance also correlates and increases with the AS defect concentration. Thus we suggest that the large χ_d and the high-field magnetoresistance both originate from the magnetic frustration originated by AS defects. We will show that, in spite of the reduced magnetization, samples having a large AS still have a comparable and even larger MR.

2. Experimental results and discussion

Ceramic Sr_2FeMoO_6 samples were prepared as described in [4]. In short, using the appropriate solid state reaction with final firing at various temperatures (T_S) under H_2/Ar stream, samples having a controlled concentration of AS defects were obtained. In the following, samples prepared at $T_S = 1200\,^\circ$C, 1100 °C, 1000 °C, 950 °C and 900 °C will be labelled as A, B, C, D and E respectively. X-ray diffraction powder patterns were collected using a Rigaku Ru-200B diffractometer and Cu Kα radiation. Inspection of the patterns revealed that almost pure single phases of tetragonal symmetry are obtained. The most relevant trend observed in the recorded patterns is the systematic increase the diffracted intensity ratio $I(101)/\{I(200) + I(112)\}$ with rising T_S. We recall here that (101) is a superstructure spot which reflects the ordering of Fe/Mo ions at B/B′ site. Here the Miller indices are given in the common $\sqrt{2}a_p$, $\sqrt{2}b_p$, $2c_p$, basis, where (a_p, b_p, c_p) correspond to the perovskite unit cell.

Detailed quantitative Rietveld analysis of the patterns was also used. Fits can be successfully done using the $I4/mmm$ space group. We shall mention here that the quality of fits using the $I4/mmm$ or the $P4/mmm$ space groups are very similar and do not allow conclusive discrimination between the groups. However, recent experiments using synchrotron radiation appear to favour the $I4/mmm$ symmetry [11]. The AS defect concentration AS can be determined by allowing the occupation of Fe and Mo ions in both sets of positions to be varied. $AS \approx 2\%$, 4.5%, 9%, 12.6% and 17% are obtained for samples A, B, C, D and E respectively [4].

The magnetization of the samples has been measured by using the Quantum Design PPMS system up to 9 T. Such large fields are required for proper analysis of the approach to saturation. In figure 1(a) we show the magnetization versus field curves $M(H)$ recorded at 10 K for samples sintered at distinct temperatures. As discussed in [4] it is clear that when increasing the disorder (AS) the magnetization indeed decreases. Moreover, detailed inspection of the magnetization data in figure 1(a) (see inset) also reveals that the samples become harder to saturate as AS rises and develop a substantial differential susceptibility χ_d that increases with AS. This is illustrated in figure 2 where we show (solid squares, left axis) the dependence of χ_d, extracted from the linear fit of $M(H)$ curves for $4\ \mathrm{T} < H < 9\ \mathrm{T}$, on AS.

The normalized field-dependent resistivity $MR = R(H)/R(H = 0)$ for some samples is shown in figure 1(b). Inspection of data in this figure immediately reveals some interesting features. First, in spite of the fact that M_S is reduced by about ∼16% from sample A to sample C, the MR is larger in the later one, particularly in the high-field region. This observation indicates that ideal Sr_2FeMoO_6 samples having fully ordered Fe/Mo sublattices may not be a pre-requisite for materials suitable for spin devices. Second, data of figure 1(b) also reveals that for none of the samples does $MR(H)$ saturate at the largest fields. It should be stressed that this behaviour is commonly found for all Sr_2FeMoO_6 samples reported so far, irrespective of their being ceramic samples or bicrystalline junctions [1, 6, 7]. It is remarkable that at high field, the slope of $MR(H)$ becomes larger for samples of smaller M_S. This behaviour can be better appreciated in figure 1(b) (inset) where we include the numerical derivative $1/R(\mathrm{d}R/\mathrm{d}H)$ versus H for some samples. The comparison of the $1/R(\mathrm{d}R/\mathrm{d}H)$ (evaluated at 50 kOe) versus AS and χ_d versus AS data in figure 2 illustrates that when AS is raised, the saturation magnetization lowers and there is a progressive enhancement of the high-field magnetization and the corresponding $1/R(\mathrm{d}R/\mathrm{d}H)$ in these double perovskites.

The MR response associated to the granular nature of the samples, which is well known to be dominant in the low-field region [12], is reflected in the low-field drop of the resistance. Inspection of data in figure 1(a) indicates that the low-field MR is significantly larger for sample C than for sample A: i.e., when reducing the synthesis temperature the low-field MR increases. This behaviour is believed to be related to the smaller grain size of sample C compared with that of sample A. Indeed, scanning electron microscopy images of both samples indicate that mean grain size varies from 1–2 μm for sample C to 2–10 μm for sample A, and it has been shown that the low-field MR becomes more prominent in samples of reduced grain size [13]. Recently, García-Hernández *et al* [14] reported a study of the low-field MR (LFMR) of a series of FeMo double perovskites. They found that the LFMR lowers when increasing the AS disorder. The MR $R(H)$ (figure 1(b)) of our samples, which indeed correspond to their high-M_S range, do not show a clear separation between the LFMR and the high field, so accurate comparison with the results of [14] is difficult. In spite of this, it is clear in figure 1(b) that at any field, the MR is larger for the samples of higher AS, thus suggesting that the general trend of the MR on AS may be subtler than suggested [14].

In addition we mention that, in nanometric size manganites, it was found [13] that the $MR(H)$ curves display a significant high-field slope which accompanies the differential

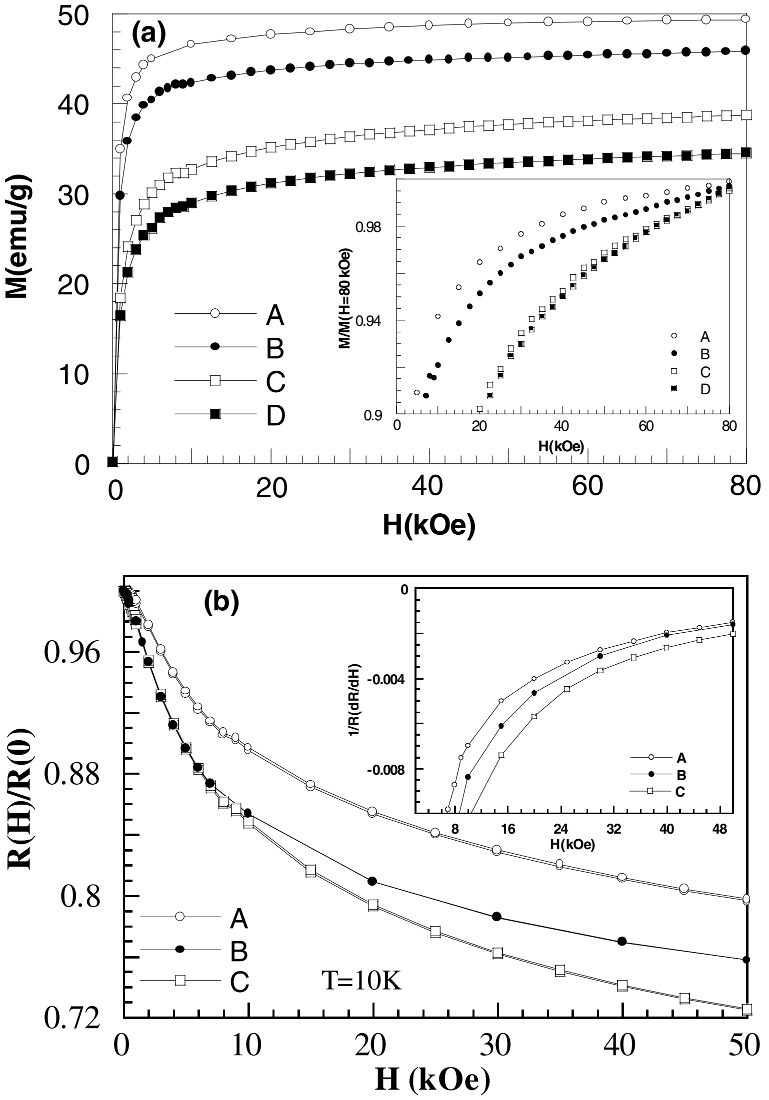

Figure 1. Magnetization (a) and normalized resistance $R(H)/R(H = 0)$ (b) versus magnetic field H at 10 K for some selected samples. Inset in (a): normalized magnetization $M(H)/M$ (80 kOe) curves. Inset in (b): numerical derivatives: $1/R(\mathrm{d}R(H)/\mathrm{d}H)$ versus H of the $MR(H)$ curves.

susceptibility χ_d. Although to some extent this behaviour is comparable to that observed in figure 1(b), it should be noticed that the grain sizes of our samples, as observed in scanning electron microscope images, are in the micrometre range and thus effects associated to surface magnetism should not be expected [13]. As a consequence, the high-field behaviour of the $MR(H)$ and the $M(H)$ shall not be attributed to grain size effects. On the contrary, the enhanced high-field susceptibility and high-field $MR(H)$ slope are very similar to that reported for $La_{2/3-x}Y_xCa_{1/3}MnO_3$ perovskites [15], where the presence of Y promotes some magnetic frustration [15, 16].

The observation of an increasingly large differential susceptibility and high-field MR could reflect the fact that AS defects, i.e. the miss-site occupancy of $Fe^{2+/3+}$ ions at $Mo^{1+/0+}$ sites,

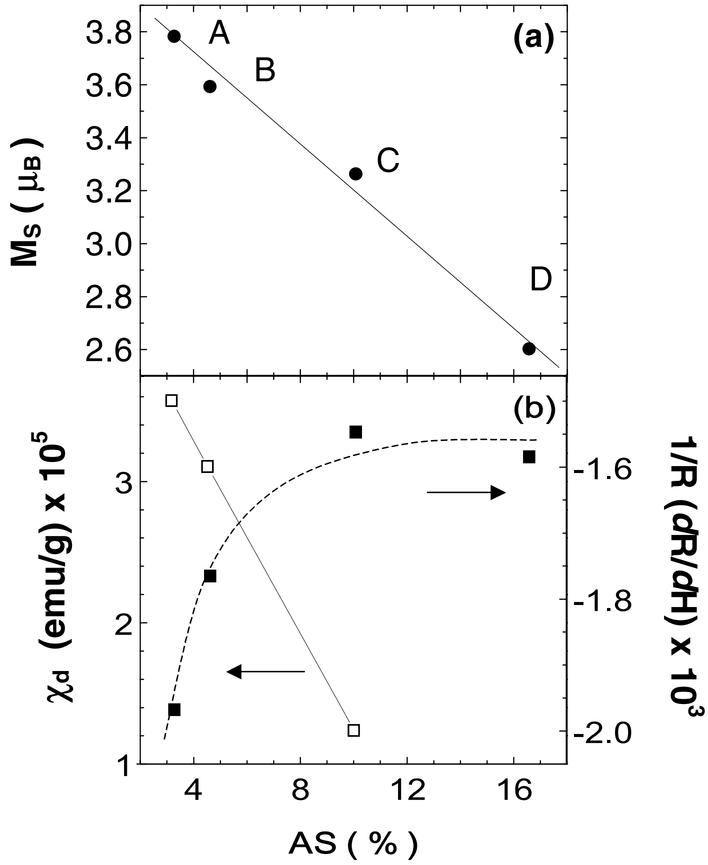

Figure 2. Dependence of the high-field differential susceptibility χ_d (left axis-solid squares) and the slope of $1/R(\mathrm{d}R/\mathrm{d}H)$ (right axis, open squares) at 50 kOe and 10 K for all samples.

have suppressed, to some extent, the collinear alignment of atomic moments within B and B′ sublattices, thus signalling the existence of some AS-defect-induced magnetic frustration. Field progressively promotes the collinear spin ordering. At this point it may be useful to recall that within the simplest superexchange coupling scenario [3] randomly misplaced Fe ions at Mo sites and *vice versa* are not expected to induce a substantial magnetic frustration. This is illustrated in figure 3 where the effects of Fe/Mo antisites in a single atomic chain is depicted. According the Goodenough–Kanamori rules, the d^5:d^1 and d^5:d^5 superexchange interactions are all antiferromagnetic, and thus atomic antisite defects do not appear to induce any frustration. This simple observation indicates that, if the observed high-field susceptibility were due to the increased AS defect concentration, then the dominant magnetic interactions should not be of nearest neighbour antiferromagnetic superexchange. Consequently, the origin of the ferrimagnetic model used to describe the spin arrangement in Fe and Mo sites should be revised. Indeed, recent measurements of the high-temperature magnetic susceptibility have clearly indicated that the dominant interactions are ferromagnetic [10]. Our finding that the χ_d systematically rises with AS is fully consistent with this.

As mentioned above, it has been suggested that APBs in double perovskites should be a common defect that may act as strongly pinned magnetic domain walls [9]. In that case,

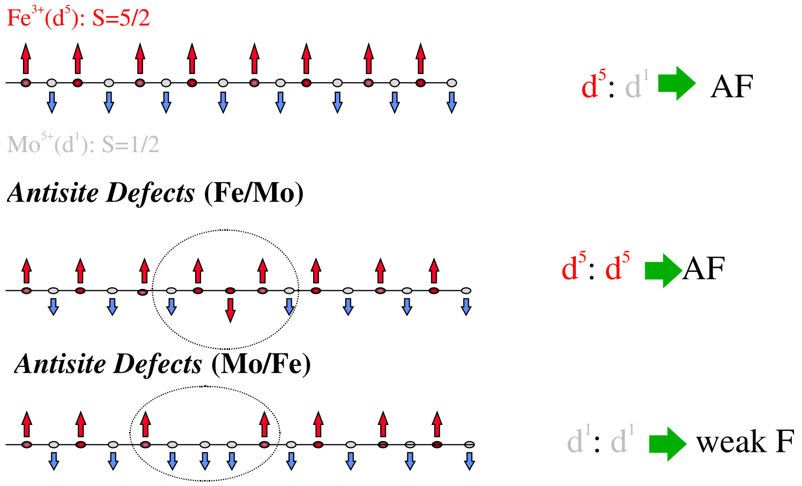

Figure 3. Schematic illustration of the superexchange magnetic coupling in Sr_2FeMoO_6 in the presence of random AS Fe/Mo defects. AF stands for antiferromagnetic interactions.

one should also expect that the approximation to saturation becomes harder in presence of APBs. In order to search for APBs, HREM observations of two samples—the almost fully Fe/Mo ordered (sample A) and the one prepared at the lowest temperature and thus partially Fe/Mo disordered (sample E)—have been performed. A Philips CM30 microscope operated at 300 kV was used. No relevant structural differences between the samples could be observed, in agreement with the x-ray diffraction analysis. However, HREM imaging indicated that sample E—prepared at lower temperature—is typically more defective than sample A.

In figure 4(a) we show a HREM image of sample E taken along the [111] zone axis. Prominent bright planes correspond to the {011} planes. A Fourier-filtered image of the boxed area obtained by selecting the (011) and $(0-1-1)$ spots in the Fourier transform is presented in figure 4(b). This image clearly shows a meandering APB across which the (011) fringes are shifted by $1/2d(011)$. Interestingly, looking at the cation sublattice of the crystal structure one finds that in a fully ordered Fe/Mo phase, a slab of thickness $d(001)$ is built by a stack of monoatomic layers of the type Fe–Sr–Mo–Sr–Fe. Therefore, a $1/2d(011)$ shift causes an exchange between the Fe(Mo) and Mo(Fe) layers across the APB as schematically illustrated in figure 4(c). The existence of some partial Fe/Mo disorder in sample E (notice that AS is only $\sim 17\%$) simply implies that the contrast between Fe(Mo) and Mo(Fe) rows as observed in the HREM images is somewhat reduced.

From the HREM analysis we should conclude that the density of APBs is rather low; in fact, in spite of the large number observations made on sample A, we failed to detect any APB in this sample. Therefore, from our data we cannot infer that APBs play a relevant role on the magnetotransport properties. Recently, Greneche *et al* [17] were led to the same conclusion from an estimation of the density of Fe ions at APBs obtained from Mössbauer spectroscopy.

In summary, we have found that the Sr_2FeMoO_6 ceramics display a differential susceptibility and a high-field MR that becomes progressively more important for samples prepared at lower temperatures and thus having a higher AS concentration. We have argued that these behaviours may reflect some magnetic frustration originated from AS defects and this could be a signature of the double exchange nature of the ferromagnetic interactions in these oxides. Of the highest significance for some applications is the observation that in highly

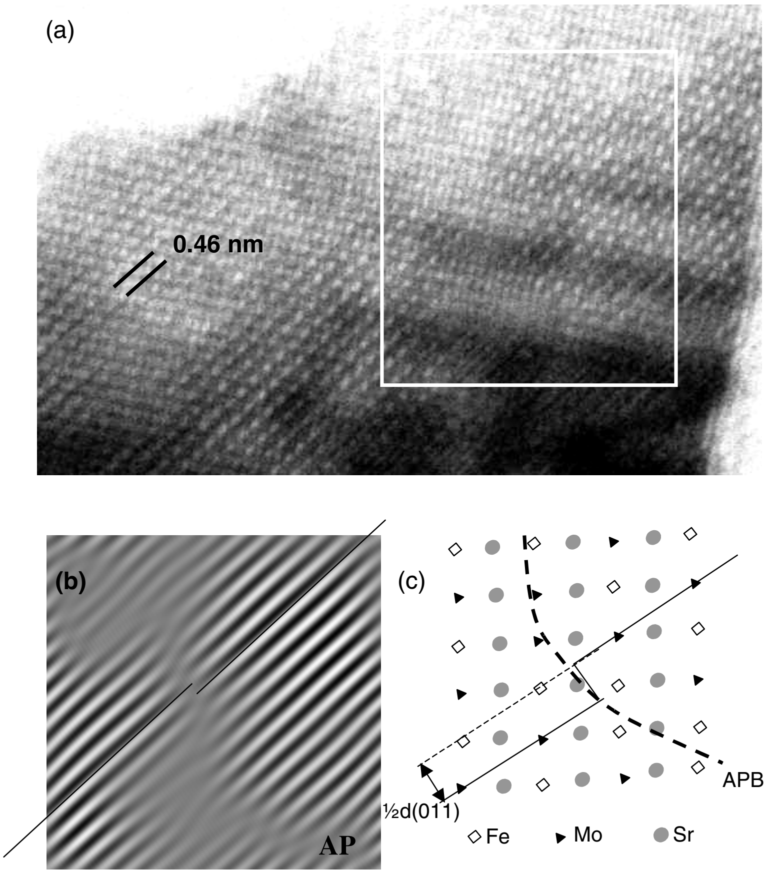

Figure 4. (a) HREM image of showing the atomic structure of sample E viewed along the [111] zone axis. (b) Fourier reconstruction of the boxed area in (a) using the (011) and $(0-1-1)$ spots, clearly revealing an APB. (c) Schematic illustration of the atomic structure at the APB. Solid lines across the APB are guides to the eyes to emphasize the $1/2d(011)$ shift.

AS-defective sample, the high-field MR is enhanced. We have been able to observe, for the first time, APBs in these double perovskites. Although the possible role of such defects on the magnetotransport properties cannot be definitely excluded, they tend to be scarce and they may not promote a substantial modification of the MR of samples.

Acknowledgments

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