Intrinsic and extrinsic inhomogeneities in mixed-valence manganites*

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It is suggested that extrinsic inhomogeneities in mixed-valence manganites deserve more attention and that they should be taken into account on equal footing with the hypothetical phase separation when examinating experimental data and developing theoretical models for the influence of stoichiometric and other types of inhomogeneities on the properties of these and other transition-metal oxides. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1739164]

The structural, magnetic, and electron transport properties of mixed-valence manganites of the type $R_{1-x}A_xMnO_3$ (where R is a rare-earth element and A is a divalent alkaline-earth element) have attracted much attention in the scientific community in the last decade (see reviews[1–6]). That interest has been stimulated by the observation of huge negative magnetoresistance (MR) near the Curie temperature T_C of the paramagnetic–ferromagnetic transition for manganites with $0.2 \leqslant x \leqslant 0.5$. This phenomenon has been called ''colossal'' magnetoresistance (CMR) and is expected to be used in advanced technology. The unique properties of mixed-valence manganites are determined by complex spin, charge, and orbital ordered phases, and are therefore of great fundamental interest for the physics of strongly correlated electrons. At the present time it is believed that one of the key feature of manganites is their intrinsic inhomogeneities in the form of coexisting competing ferromagnetic and antiferromagnetic/ paramagnetic phases.[3,4,6] This phenomenon is generally called ''phase separation.'' In Refs. 3 and 6, theoretical computational models were developed for two cases: 1) electronic phase separation, which implies nanocluster coexistence; 2) disorder-driven phase separation, which leads to rather large (micrometer size) coexisting clusters. Existence of the nanoscale as well as micrometer-size inhomogeneities in manganites has been corroborated experimentally (see Refs. 3, 4, and 6 and references therein). Some other examples of the phase-separation models can be found in Refs. 4 and 7–10 (actually, there is a vast literature on the subject, but it cannot be cited more fully in this brief communication). On this basis it is hoped that the transport and magnetoresistive properties (including CMR) of manganites can be explained with the phase separation effects taken into account.

In spite of enormous theoretical and experimental activity in the area of phase separation in manganites, many questions (sometimes rather simple and naive) remain open. Intrinsic inhomogeneities are believed to arise for thermodynamic reasons, so that relative fraction of competing phases should depend on temperature, pressure, and magnetic field. The known experimental studies give numerous (though predominantly indirect) indications of structural and magnetic inhomogeneities in manganites, but are they in all cases intrinsic? The point is that extrinsic inhomogeneities are inevitably present in all manganites (even in single-crystal samples). Extrinsic inhomogeneities arise due to various technological factors in the sample preparation. They can cause inhomogeneity in the chemical composition (first of all in the oxygen content), structural inhomogeneities (polycrystalline or even granular structure), strain inhomogeneities, and so on. It is easy to find in the literature numerous experimental studies in which the finding of phase separation effects is proclaimed, but the interpretations are often doubtful. In such cases the effects of technological inhomogeneities are quite obvious or, at least, can not be ruled out. In some cases the magnetic inhomogeneities, induced by extrinsic causes, can depend significantly on temperature, pressure, and magnetic field as well, and their apparent influence on the magnetic and transport properties of mixed-valence manganites may agree generally with that predicted by some of the numerous phase-separation theoretical models. It should be noted, however, that a quantitative comparison of the known models with experiment is practically impossible (or is too ambiguous).

Consider briefly the main sources of extrinsic inhomogeneities. Mixed-valence manganites are complex perovskite-like oxides consisting of at least four elements. Their properties are very sensitive to crystal imperfections, especially to the structural, composition and other types of inhomogeneity in the crystal lattice. The crystal perfection (and corresponding level of inhomogeneity) depends strongly on the method of preparation, and on preparation conditions for the given method. In rough outline, the following methods of manganite growth are used: 1) thin film growth (mostly with the pulsed-laser deposition method); 2) solid-state reaction method; 3) floating zone method.

Thin manganite films can be prepared in highly oriented or even single-crystal epitaxial form with a fairly perfect crystal lattice. The highest values of the magnetoresistance have been observed in thin films. But it should be taken into account that films are always in an inhomogeneous strained state due to inevitable substrate-film lattice interaction, which, as a rule, induces considerable magnetic and magnetoresistance anisotropy.[11] Due to the strained state, some other film properties (among other things, the value of T_C) can be quite different from those of bulk materials.

Consider some examples of extrinsic inhomogeneities in

films. A comprehensive and thorough study (by high-resolution electron microscopy)[12] of epitaxial $La_{1-x}Ca_xMnO_3$ ($x \approx 0.3-0.35$) films grown on $SrTiO_3$ substrates has revealed that close to the substrate a perfectly coherent strained layer is formed, above which crystal blocks with columnar structure grow; these blocks and the boundary regions between them accomodate the lattice mismatch between substrate and film. The boundary regions between blocks (domains) are nonstoichiometric, having deficiencies of oxygen and lanthanum. Similar results are reported in Ref. 13, where secondary-phase nonstoichiometric rods were found in $La_{0.7}Ca_{0.3}MnO_3$ films grown on $LaAlO_3$ and $SrTiO_3$ substrates. The films have a domain structure, in which the rods are believed to be responsible for relieving stress during film growth. Magnetic force microscopy study of pulsed-laser-deposited $La_{1-x}Sr_xMnO_3$ ($x=0.23$ and 0.3) films[14] have revealed local FM regions at temperatures above the T_C of the film. These regions with higher T_C were found around the grain boundaries and attributed to local variation of the strain in the film. The above examples show that even epitaxial films prepared under optimal conditions have inhomogeneous strains and a local nonstoichiometry that can play a significant role in the transport and magnetoresistive properties of thin films.

The solid-state reaction (SSR) technique enables preparing ceramic or polycrystalline samples. The crystal quality (and, therefore, the resistive, magnetoresistive, and magnetic properties) of the SSR samples depends in a crucial way on the preparation conditions, especially on sintering and annealing temperature. In samples prepared with optimal sintering temperature, fairly sharp resistive and magnetic transitions near T_C are observed, whereas quite different resistive and magnetization behavior is seen for samples with the same nominal composition but prepared at low temperature.[15] This is to be attributed to compositional and structural inhomogeneity of samples sintered at low temperatures. For all preparation conditions, however, SSR samples are always polycrystalline and inevitably contain at least one source of inhomogeneity: grain-boundary regions. These are regions of structural, magnetic, and stoichiometric disorder, and they therefore have different conducting and magnetic properties as compared with these inside the grains. Beside this, rather appreciable compositional inhomogeneities (not associated with grain boundaries) cannot be eliminated in SSR samples even when they are prepared under optimal conditions. The common methods of checking of stoichiometric inhomogeneity and mixed-phase state (x-ray powder diffraction or electron microprobe analysis) have too low accuracy to come to an unambiguous conclusion about composition homogeneity. For example, if a sample is a mixture of two phases of $R_{1-x}A_xMnO_3$, composed from the same elements but with appreciably different values of x or oxygen concentration, it is hard or even impossible to see clearly enough the two-phase state in a diffraction pattern, even if the volume fractions of the phases are comparable, whereas the magnetic and other properties of these phases can be significantly different. Only nonperovskite-type impurities can be detected quite clearly down to 2%. Electronic microprobe elemental analysis has an accuracy about $\pm 5\%$ in most cases, leaving room for stoichiometic disorder within these limits. More powerful, but much more expensive methods, like neutron diffraction or small-angle neutron scattering, are not in common use, but even those methods have their limits of accuracy. Since the properties of manganites are very sensitive to chemical composition and, therefore, to stoichiometric disorder, it is not surprising to find in the literature quite different properties of manganites of the same nominal composition, prepared by the SSR method. In spite of the unavoidable technological inhomogeneity, the SSR method is in common use for preparation of mixed-valence manganites of various composition. The reason is that the SSR method appears to be not very sophisticated (at least, at first glance) and does not require expensive equipment. With proper experience and rather hard work it is possible to obtain polycrystalline samples of rather good quality, with sharp resistive and magnetic transitions. For example, a generally recognized phase diagram for the system $La_{1-x}Ca_xMnO_3$ has been obtained for SSR polycrystalline specimens.[5]

It is easy to find in the literature hundreds of papers devoted to film or bulk ceramic manganites, but far fewer studies concern single-crystal samples. The obvious reason is that it is not so easy to prepare manganite single crystals. But even single crystals prepared by the floating zone method are not free from defects and extrinsic inhomogeneities. In reality, they have mosaic blocks, twins, inhomogeneous strains, and stoichiometric disorder.[16–18]

The experimental data therefore show that technological inhomogeneities are unavoidable for any preparation method, and they can actually be called ''intrinsic'' as well. For this reason, (i) in many cases it is better to speak about multiphase coexistence instead of phase separation; (ii) the technological inhomogeneities should be directly taken into account in new theoretical models. The latter demand derives from the circumstance that manganite materials which can be used in advanced technology will surely have some crystal imperfections or inhomogeneities. Moreover, in some cases specific types of inhomogeneities should even be specially induced to provide necessary properties. For example, grain boundaries or specially prepared percolation structures can ensure high MR in low fields in the temperature range far below T_C, which may be necessary for some applications.

As to phase separation, this concept has, on the one hand, now become a commonplace, while, on the other hand, the term is too general to imply anything specific. In interpreting their results, experimentalists often speak quite generally about phase separation or just mention it, meaning not much by it. And how could they, since at least a dozen diverse models (suggesting quite different mechanisms of phase separation) have been developed, which in practice, however, cannot be numerically compared with experiment? In spite of this, the phase-separation concept appears to be very attractive, since it can give a quite natural qualitative explanation for both the huge drop in resistance and the CMR in the vicinity of magnetic transitions in manganites, taking into account a percolational character of these transitions.[4,8] Consider, for example, the $La_{1-x}Ca_xMnO_3$ system. According to Refs. 19–24, the paramagnetic-ferromagnetic (PM-FM) transition in this compound is of first order for the range $0.25 < x < 0.4$. It is found in these

compounds that FM metallic clusters are present well above T_C, while some PM insulating clusters can persist down to a range far below T_C.[25–27] That seems natural for a first-order transition, where nucleation of the FM clusters above T_C is quite expected, as well as the presence of some amount of PM clusters below T_C. After all, a transition of this type is hysteretic and depends on the rate of heating or cooling. In this case real phase separation and percolation processes can be expected around T_C. Since the PM phase is insulating and the FM one is metallic, some kind of insulator-metal transition takes place near T_C. The technological inhomogeneities broaden the temperature range of the PM-FM transition, so that it may appear smoother and more continuous, like a second-order transition.

For Ca concentration outside of the above-indicated range, $0.25 \leqslant x \leqslant 0.4$, the PM-FM transition is found to be of second order in $La_{1-x}Ca_xMnO_3$ samples with $x = 0.20$, 0.40, and 0.45 (Refs. 22, 29, 30). According to the phase diagram for this system,[1,3,5,6] these concentrations are close to the critical ones: $x \approx 0.2$ (which is a border between the FM metallic and insulating states) and $x = 0.5$ (which is a border between FM metallic and insulating charge-ordered states). It is clear that unavoidable technological stoichiometric disorder will have a greater impact on the magnetic transition for samples having nominal Ca concentrations near the above-mentioned critical values. The T_C value depends rather strongly on x near these threshold concentrations, whereas the concentration dependence of T_C near the optimal doping ($x \approx 0.35$) is rather weak (see the phase diagram in Refs. 1, 3, 5, and 6). In this case, the magnetic transition for a sample with nonoptimal concentration should be broader than that for the optimally doped samples, even if the level of compositional inhomogeneity is equal in both cases. It cannot be ruled out, therefore, that a second-order transition found for these $La_{1-x}Ca_xMnO_3$ samples is just a rather broadened (smeared) first-order transition.

It should be noted that the PM-FM transition is found to be of second order in Sr-doped $La_{1-x}Sr_xMnO_3$ samples ($x = 0.3$ and 0.33) as well.[19,31] The Sr manganites are more conductive than Ca manganites and have much higher T_C (maximum T_C are about 260 K and 370 K for Ca and Sr manganites, respectively). It seems that manganites with higher conductivity and T_C are more prone to a second-order transition than those with low conductivity and T_C. In homogeneous samples with a perfect crystal lattice the second-order transition from the PM to the FM state should proceed at once in the whole sample volume as soon as the temperature crosses T_C from above. No nuclei of the FM phase above T_C and no supercooling or hysteresis phenomena should occur at this transition. Only thermodynamic fluctuations of the order parameter (the magnetization) are expected, which, however, should be confined to a narrow critical region around T_C (Refs. 32, 33). These fluctuations of the magnetic order have usually a rather noticeable effect on ''nonmagnetic'' properties such as the temperature coefficient of the resistivity, heat capacity, magnetoresistance, and thermal expansion in the vicinity of T_C (Refs. 32, 33).

Stoichiometric disorder and inhomogeneous strains of the crystal lattice, which are unavoidable in real manganites due to the above-indicated technological reasons, can undoubtedly have a pronounced effect on the second-order PM-FM transitions. This effect has long been known and considered for simple FM metals.[33] Take, for example, as in Ref. 33, a system consisting of multiple phases with different T_C. There is some volume distribution of regions with different T_C within the sample. The presence of interphase transition regions between different phases should be taken into account as well. The temperature dependence of the magnetization for this sample will show a somewhat broadened PM-FM transition[33] (the temperature width of the transition depends on how wide is the distribution of T_C in the sample). From that an averaged T_C value can be determined. But some parts of the sample have T_C greater or less than this averaged value. Therefore, it can be found by some experimental methods that some FM clusters exist above T_C, their volume increasing as T_C is approached from above, while PM clusters can be found below T_C, their volume fraction decreasing as the temperature decreases away from T_C. The reason for this behavior is quite obvious when the sample inhomogeneity is taken into account. Now, even if every single phase of this multiphase system undergoes a second-order transition, the total character of the transition will not be that for the homogeneous system. It will be of a percolational nature. If the PM and FM phase states differ drastically in their conductivity, CMR can be found. Imagine that the size of the inhomogeneities is rather small, say, a few nanometers (which is quite possible for technological inhomogeneities). Is it possible in this case to attribute with any certainty the magnetotransport behavior of this system near the PM-FM transition to the phase separation effect? The negative answer is obvious, since technological inhomogeneities can by themselves provide this behavior.

Due to enormous theoretical activity in this area, it is rather appropriate to believe that phase separation really takes place in manganites and in other transition-metal oxides (although it is difficult to make the right choice among the numerous proposals for the phase separation mechanisms). But how can one reliably enough distinguish these thermodynamic effects from those of extrinsic inhomogeneities? That is a really difficult problem. I think that theoreticians should not disregard the influence of extrinsic inhomogeneities, but, on the contrary, they should take them into account in their models quite directly along with intrinsic inhomogeneities. This necessity was indicated quite clearly in the paper by Yukalov.[10] One of the principal ideas of that paper is that real systems are never free from external perturbations, and that makes the system stochastically unstable even if the external perturbations are infinitesimally small. After all, extrinsic inhomogeneities can even stimulate the appearance of thermodynamic phase separation, so that some kind of interaction between them is possible.

In conclusion, when considering the experimental data for mixed-valence manganites and developing theoretical models for them, the unavoidable influence of extrinsic disorder and inhomogeneities should always be taken into account. These inhomogeneities can act separately as well as together with the suggested intrinsic inhomogeneities (phase separation) and determine to a great extent the magnetic and magnetotransport properties of these compounds. Although, for the most part, the known properties of the

$La_{1-x}Ca_xMnO_3$ system near the PM-FM transition have been used here in support of the above-mentioned point of view, the general conclusion of this paper is applicable (in the author's opinion) to other magnetic transitions in manganites (for example, for transitions to charge-ordered states) and to related magnetic transition-metal oxides, such as the cobaltites $La_{1-x}Sr_xCoO_3$.

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*This paper does not fit in with any of the permanent rubrics of this journal. It is actually better suited to a category such as "Critical reviews" or "Viewpoint" that some journals offer. In his paper, B. I. Belevtsev (on the strength of the analysis of published experimental and theoretical works) considers the important and topical question of the influence of intrinsic and extrinsic inhomogeneities on the properties of mixed-valence manganites with colossal magnetoresistance. The editors have decided to publish Belevtsev's paper in the hope that it will be of interest to our readers.

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