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Colossal Magnetoresistance in La-Ca-Mn-O

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Very large change in electrical resistivity by several orders of magnitude is obtained when an external magnetic field is applied to the colossal magnetoresistance (CMR) materials such as La-Ca-Mn-O. The magnetoresistance is strongly temperature-dependent, and exhibits a sharp peak below room temperature, which can be shifted by adjusting the composition or processing parameters. The control of lattice geometry or strain, e.g., by chemical substitution, epitaxial growth or post-deposition anneal of thin films appears to be crucial in obtaining the CMR properties. The orders of magnitude change in electrical resistivity could be useful for various magnetic and electric device applications.

Introduction

The recent discovery of colossal magnetoresistance (CMR) phenomenon in doped manganites, which exhibit a field-induced change in electrical conductivity by many orders of magnitude, has stimulated much research in the field,[1-15] especially in view of technical interest in magneto-electronics[16] and spin-polarized transport devices.[17,18]

Perovskite-like oxide of lanthanum manganite ($LaMnO_3$) exhibits both strong ferromagnetism and metallic conductivity when La ions (3+ valence) are partially substituted with 2+ valence ions such as Ca, Ba, Sr, Pb and Cd. This results in a Mn^{3+}/Mn^{4+} mixed valence state creating mobile charge carriers and canting of Mn spins.[19-28] In the unit cell of a perovskite ABO_3, A at the corners of the cube represents a large ion such as La^{3+}, Nd^{3+}, Pr^{3+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}, B at the center of the cube stands for a small ion such as Mn^{3+}, Mn^{4+}, Cr^{3+}, Fe^{3+}, Ti^{4+}, and O at the center of the faces represents O^{2-}. The Mn ions are surrounded by oxygen octahedra. The ionic radii of the elements pertinent to the manganites are listed in Table I. These elements form either simple $AMnO_3$ type or mixed (A+A') (B+B') MnO_3 type perovskites following Goldschmidt's perovskite stability criterion on ionic radii, i.e., the ratio $(r_A+r_0)/(r_B+r_0)\sqrt{2}$ should be approximately unity. (r_A, r_B+r_0 represent the radii of ions A, B, and O, respectively).

The CMR manganites exhibit very large magnetoresistance (MR) ratios (defined here as $\Delta R/R_H = (R_H-R_0)/R_H$ where R_0 is the zero field resistance and R_H is the resistivity in the applied magnetic field, e.g., H = 6T) as compared to the giant-magnetoresistance (GMR) type materials of metallic multilayer or heterogeneous films[29-35] with the MR values typically in the range of 5-150%. In this article the electrical, magnetic and magnetoresistance behavior in epitaxial La-Ca-Mn-O and La-Y-Ca-Mn-O films with extraordinary MR values as high as 10^{9}% will be described.

The Occurrence of Colossal Magnetoresistance

The CMR phenomenon is qualitatively explained in terms of the double exchange process in a hole-doped manganite where the electron hopping between the Mn^{3+} and Mn^{4+} ions becomes easier in a magnetic field. The paramagnetic-to-ferromagnetic (or semiconductor-to-metallic) transition temperature (T_c) is raised in a field, thus at a given temperature the material can be shifted between the low and high conductivity state sometimes with a colossal magnitude.

Not all rare earth manganites exhibit the CMR behavior. For CMR (which is arbitrarily defined here as MR>1000% or a ten-fold increase in conductivity), the manganite composition should be such that preferably a cubic perovskite structure (and a conductive/ferromagnetic regime) is present, for example, a stoichiometry of $La_{1-y}Ca_yMnO_3$ or $Pr_{1-y}Ca_yMnO_3$ with y in the range of about 0.3-0.5. The lattice dimension(Mn-O-Mn bond length and bond angle) should also be appropriately adjusted either by chemical substitution of cations[7,10-12] epitaxial control of lattice strains,[14] or processing-dependent control of other

parameters possibly including the anion stoichiometry. While the $La_{0.67}Ca_{0.33}MnO_x$(x ~ 3.0) epitaxial film exhibits the CMR behavior, a similar compound stoichiometry containing Ba or Sr[1,8,10] instead of Ca does not exhibit the CMR properties because of their much larger ionic radii (see Table I). If the $La_{0.67}Ca_{0.33}MnO_x$ compound is in the bulk ceramic form instead of the film form, the CMR behavior is lost, with the magnetoresistance well below ~ 1000%.[1] Even among the thin films of La-Ca-Mn-O, only the epitaxially grown films (e.g., $La_{0.67}Ca_{0.33}MnO_x$ on a single crystal $LaAlO_3$ substrate with a closely matching lattice parameter) exhibit CMR. The La-Ca-Mn-O films deposited on substrates with non-matching lattice parameters such as MgO, Al_2O_3, YSZ or Si generally do not show the CMR properties.[1,9]

Magnetotransport Properties

La-Mn-Ca-O and La-Y-Ca-Mn-O films, 100-5000Å thick, were deposited on (100) $LaAlO_3$ substrates by pulsed laser deposition (PLD). The substrate temperature was about 700°C, and the oxygen partial pressure in the chamber was maintained at 100-300 milliTorr. The nominal target compositions were $La_{0.67}Ca_{0.33}MnO_x$ and $La_{0.60}Y_{0.07}Ca_{0.33}MnO_x$. The chemical composition of the deposited film was found to be similar to that of the bulk target used for the deposition by scanning electron microanalysis and Rutherford backscattering analysis. X-ray diffraction and rocking angle analysis as well as transmission electron microscopy indicate that the La-Ca-Mn-O films have the perovskite-type cubic structure with a lattice parameter of a ~ 3.87 Å and grow epitaxially on the $LaAlO_3$ substrate (a = 3.79Å).

The electrical resistance and magnetoresistance of the films were measured as a function of temperature and magnetic field by four technique (using a constant current) in a superconducting magnet with the maximum applied field of H = 6-7 Tesla. For most of the films, the field direction was parallel to the current direction. Some of the measurements were carried out with the field applied perpendicular to the current direction in the film (either by in-plane field or perpendicular filed). The MR behavior in the La-Ca-Mn-O and La-Y-Ca-Mn-O films is almost always negative and essentially isotropic with respect to the field direction if the demagnetizing factor is taken into consideration. The M-H loops were obtained by using a vibrating sample magnetometer with the maximum field of H = 1T.

The La-Ca-Mn-O film (~1000Å thick) in the as-deposited condition exhibits a MR ratio of 500-40,000% (at 100 K, H = 6 T) depending on the deposition conditions. Subsequent heat treatment at 850°C /1 h in a 3 atm oxygen atmosphere dramatically improves the MR ratio to 1.1 × 10^6%(at 110 K, H = 6T).

In Fig. 1, the resistivity versus field curve for the heat treated La-Ca-Mn-O film at 110 K is shown. The figure shows that the major part of the resistivity drop occurs at H < 2 T. The zero-field resistivity of ρ = 50.8Ω cm (resistance R = 4.13 MΩ) is reduced to ρ = 4.61 mΩ·cm (R - 375Ω) when the in-plane applied field (parallel to the direction of the applied current) is increased to 6 T. These samples, both the as-deposited and the heat treated films, exhibit higher MR ratios than our previous samples.[1] The general trend that we observed is that denser and more uniform targets (e.g., sintered at higher temperatures and longer times) produce better quality films with improved epitaxy, less particulate incorporation, better chemical homogeneity and thickness uniformity, thus exhibiting higher MR values.

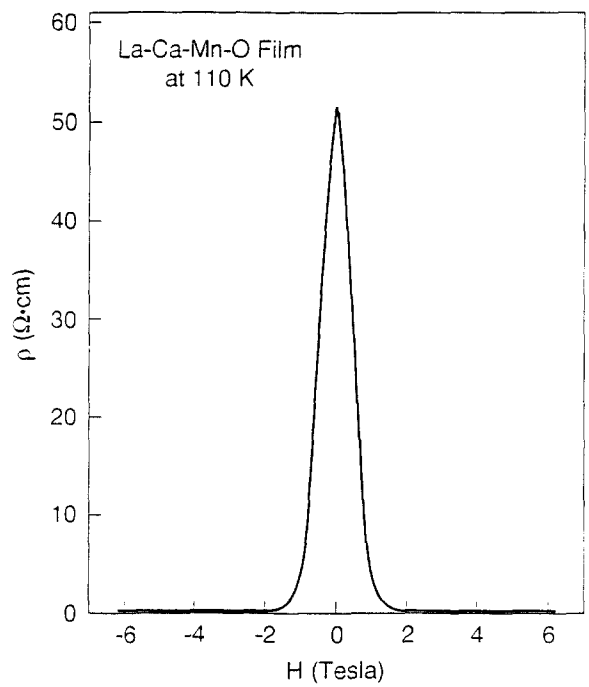

Fig. 1 Resistivity vs field curve for the La-Ca-Mn-O film at 110K.

Interestingly, the magnetoresistance in the La-Ca-Mn-O films exhibits a strong dependence on film thickness.[14] The maximum MR occurs at a film thickness of ~1000Å, with the MR ratio of 1.1 million %. The MR ratios for the films thinner or thicker than about 1000Å are drastically lower. The MR values are ~1700% for 2000Å and ~1400% for the 5000Å thickness. The films substantially thinner than ~ 1000Å also exhibit decreased MR ratios, e.g., ~21,000% for 500Å thickness and 2200% for 100Å thickness. It is hypothesized that the observed thickness dependence of MR is related to the change in the lattice strain induced by the change in film thickness. In the $La_{0.67}Ca_{0.33}MnO_x$ material the colossal magnetoresistance (>100,000%) is generally obtainable, not in a polycrystalline form, but only in epitaxially grown films on single crystalline $LaAlO_3$ with a lattice parameter of ~3.79Å, smaller than that of the bulk

La-Ca-Mn-O materials (a ~3.867Å). Thus it is quite possible that the very large magnetoresistance observed is directly related to the optimal straining of the lattice, i.e., compressively by the epitaxy imposed by the substrate with the smaller lattice parameter.

Shown in Fib. 2 are the temperature dependence characteristics of ρ, $\Delta R/R_H$ and M of a $La_{0.67}Ca_{0.33}MnO_x$ film which was heat treated at 900°C and exhibits ~120,000% MR effect. As is evident in the figure, the ρ vs T curve exhibits a relatively sharp cusp at ~ 95K with the film showing the semiconductor behavior (i.e., a negative dρ/dT) above and the metallic behavior (a positive dρ/dT) below this temperature. The temperature at which the magnetoreistance ($\Delta R/R_H$) of the film is maximum is almost invariably located in the metallic-behavior region on the left (low temperature) side of the resistivity peak. It is interesting to note that the magnetoresistance peak occurs at the temperature where the resistivity is roughly one-half of the peak resistivity or near the inflection point of the curve. The mechanism(s) responsible for the very large

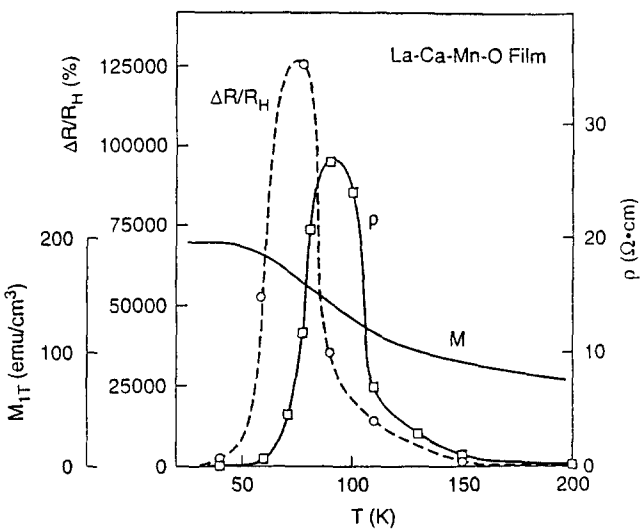

Fig. 2 ρ, $\Delta R/R_H$ and M vs T curves for the epitaxial La-Ca-Mn-O film.

magnetoresistance observed in the La-Ca-Mn-O film appear(s) to be related to the semiconductor-to-metal transition, however, the exact mechanism(s) are not clearly understood at the moment.

Also shown in Fig. 2 is the magnetization M (at H = 1T) vs temperature curve for the La-Ca-Mn-O film. It is evident that the film is strongly ferromagnetic with M ~ 200 emu/cm^3 at 50K and M ~ 100 emu/cm^3 at 150K. The M-H loops measured below the magnetic transition (Curie temp.) exhibit magnetic hysteresis with a coercivity (H_c) of about 30-50 Oe.

For many practical applications, magnetoresistance near room temperature and in low fields is desirable. As the CMR manganites generally exhibit very large MR at low temperatures and high applied fields, it remains a challenge to make the CMR occur at room temperature and in practical low field ranges. The temperature at which the MR is maximum can be altered, e.g., to near room temperature adjusting compositional or processing parameters. However,

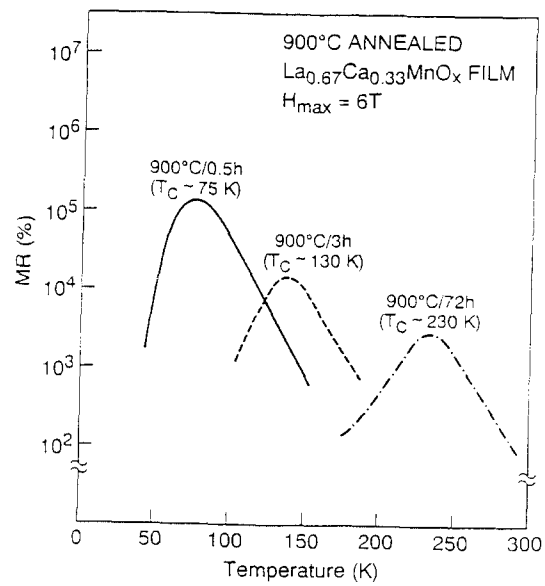

Fig. 3 Magnetoresistance behavior of the $La_{0.67}Ca_{0.33}MnO_x$ film as altered by post-deposition heat treatment.

this happens at the expense of the MR value. For example, a La-Ca-Mn-O film deposited at a higher oxygen partial pressure of ~ 300 milliTorr gives near room temperature MR of ~ 1300% at 260K and ~ 470% at 280K. Shown in Fig. 3 is the change in the MR behavior of the La-Ca-Mn-O film after various post-deposition annealing heat treatment in an oxygen atmosphere. As is evident from the figure, the maximum MR of the film can be made to occur at a different temperature by adjusting the annealing treatment.

Such an adjustment of MR behavior can also be accomplished by compositional modifications, for example, with a partial substitution of Ca with Sr in La-Ca-Mn-O. The R vs H curve for a $La_{0.55}Ca_{0.25}Sr_{0.08}MnO_x$ film at room temperature (ρ ~1.4mΩ·cm), as shown in Fig. 4, is approximately linear with an MR ratio of 2.5% at H ~ 500 Oe (equivalent to about 0.05% MR for a lower field of ~ 10 Oe (this is about the level of field strength of interest for magnetic recording read heat)). However, as the electrical resistance of this oxide film is about two orders of magnitude higher than that of the 80%Ni-20%Fe permalloy (with the MR ratio on the order of 3% for H = 10 Oe), the field sensing output voltages turn out to be comparable for the two materials at the same level of sensor current. For a constant current of 1-10 mA, the ΔV voltage signal from this unoptimized film for H = 10 Oe would be 0.13-1.3 mV, comparable to the ΔV value from the permalloy film with the same dimension. The lower resistivity of the permalloy,

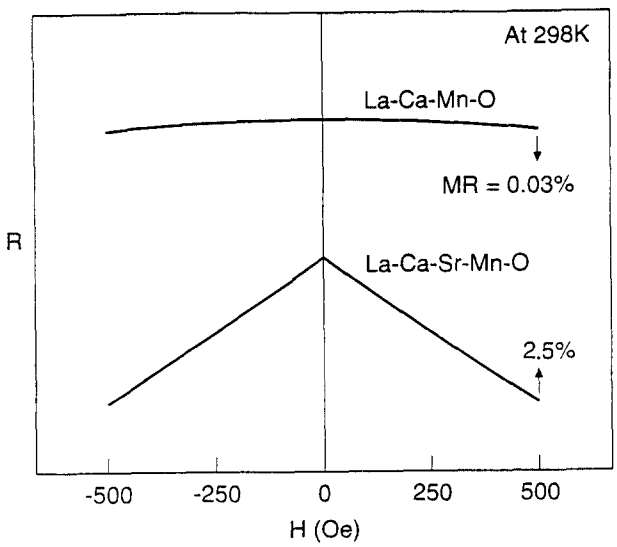

Fig. 4 R vs H curve for the La-Ca-Sr-Mn-O film.

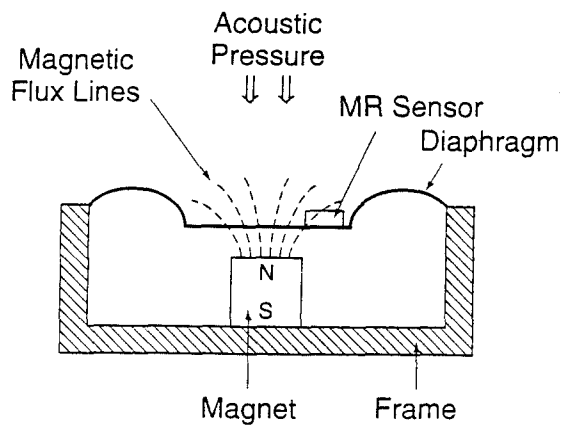

Fig. 5 A magnetoresistive microphone design.

however, is an advantage in terms of the ease of device design.

The magnetoresistive properties fo the La-manganite films can be used for a number of other applications. An example is a magnetoresistive microphone design such as schematically illustrated in Fig. 5. A small, La-Ca-Sr-Mn-O type MR sensor, about 2 × 4 mm size was mounted on a plastic diaphragm. As sound waves with varying intensity hit the diaphragm and make it vibrate, moving the MR sensor in relation to the magnet that supplies a gradient field. The resulting change in the magnetic field intensity on the sensor causes change in resistivity, which in turn changes the output voltage ΔV. The sensor signal, many millivolts even in the unamplified condition, decreases with the distance from the sound as is expected.

Recent data on epitaxial films of $La_{0.60}Y_{0.07}Ca_{0.33}MnO_x$ on $LaAlO_3$ substrate give much higher MR values (as large as 10^9%) than the undoped La-Ca-Mn-O films. The change in

Table I. Ionic radii of elements involved in perovskite-like manganites

Ion	La^{3+}	Pr^{3+}	Nd^{3+}	Sm^{3+}	Gd^{3+}	Y^{3+}		
Radius(Å)	1.22	1.16	1.15	1.13	1.11	1.06		
Ion	Ca^{2+}	Sr^{2+}	Ba^{2+}	Cd^{2+}	Pb^{2+}	Mn^{3+}	Mn^{4+}	O^{2-}
Radius(Å)	1.06	1.27	1.43	1.03	1.32	0.70	0.52	1.32

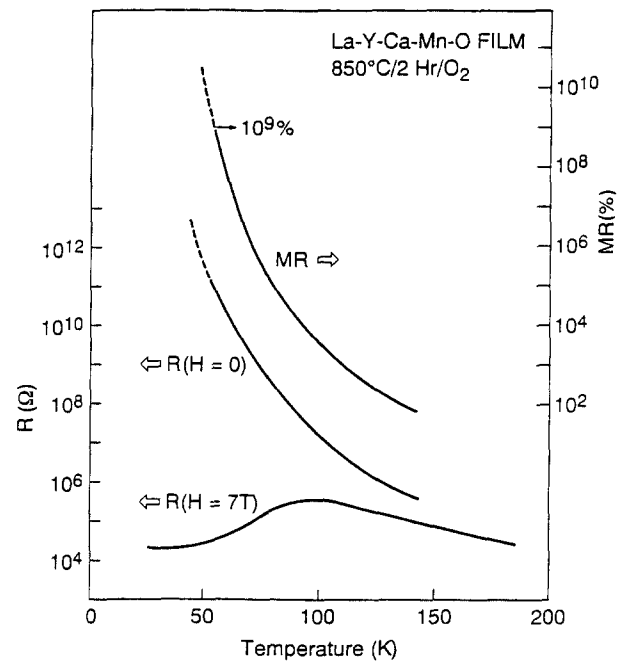

Fig. 6 R and MR vs T curve for the La-Y-Ca-Mn-O film.

lattice parameter affects the interatomic distance and bond angle, thus influencing the magnetic exchange interactions between two magnetic cations. As listed in Table II, the Y-doping[10] of La-Ca-Mn-O compound decreases the lattice parameter *a* from 3.867 A to 3.859 A, due to the smaller cation radius of Y^{3+} of 1.06 A as compared to that of La^{3+} (1.22A). Thus, the effect of lattice parameter decrease by Y-doping is superimposed on the similar effect of epitaxial growth on a smaller lattice substrate ($LaAlO_3$ in this case), and results in a further improvement in colossal

Tabel II. MR values (at H = 6T, T = 70-140K) and lattice parameters for La-Ca-Mn-O and La-Y-Ca-Mn-O.

	LCMO	LYCMO
Cation Radius	$r(La^{3+}) = 1.22$	$r(Y^{3+}) = 1.06$Å
Lattice Parameter	a = 3.867	a = 3.859Å
MR(Bulk Materials)	500%	104%
MR(Epitaxial Films)	10^6%	23 x 10^6%

magnetoresistance in the La-Y-Ca-Mn-O film. As a result, the CMR effect is much higher in the La-Y-Ca-Mn-O films than in the La-Ca-Mn-O films. It is also interesting to note from Table I that both in bulk materials and epitaxial films, the MR ratio of La-Y-Ca-Mn-O system is roughly ~20 times higher than that of La-Ca-Mn-O system. These results indicate that the lattice engineering seems to be a key to obtaining a large CMR effect.

The temperature dependence of resistance and MR ratio in the La-Y-Ca-Mn-O film is shown in Fig. 6. The MR ratio (at a slightly higher applied field of 7 T) is about 500% at 130 K, which progressively increases to ~10^9% at ~ 50K. Below about 50K, due to the measurement limit of the electrometer used, the magnetoresistance could not be accurately measured. However, considering the trend in MR vs T curves in Fig. 6, it is likely that the magnetoresistance ratio of the La-Y-Ca-Mn-O films is at least a few orders of magnitude higher than 10^9%. These MR values are the highest ever reported for the La-Ca-Mn-O based films.

Summary

Colossal magnetoresistance as high as 10^9% has been obtained in epitaxially-grown, single crystallien La-Ca-Mn-O and La-Y-Ca-Mn-O films. The magnetoresistance behavior appears to be related to the semiconductor-to-metal transition which is affected by lattice geometry, chemical composition and material processing. Ordinary materials obey the well known Ohm's law, V=IR, with a finite value of R. In supereonductors, R is essentially zero and hence an enormous amount of current can flow up to the critical current level. In the CMR materials, R is not a constant but a tunable quantity. The fact that the electrical conductivity of the material can be manipulated by applied field to a value orders of magnitude different could be exploited for various technical applications. It remains a challenge to bring about the CMR phenomenon at room temperature and in low fields for practical use.

References

[1] S. Jin, T. H. Tiefel, M. McCormack, R.A. Fastnacht, R. Ramesh, and L. H. Chen, Science **264**, 413 (1994).

[2] S. Jin, M. McCormack, T. H. Tiefel, and R. Ramesh, J. Appl. Phys. **76**, 6929 (1994).

[3] B. Raveau, A. Maignan, and V. Caignaert, J. Sol. State Chem. **117**, 426 (1995).

[4] H. L. Ju, C. Kwon, Q. Li, L. Green and T. Venkatesan, Appl. Phys. Lett. **65**, 2109 (1994).

[5] G. Gong, C. Canedy, G. Xiao, J. Sun, A. Gupta, and W. J. Gallagher, Appl. Phys. Lett. **67**, 1783 (1995).

[6] S. K. Singh, S. B. Palmer, D. McK. Paul, and M. R. Lees, Appl. Phys. Lett. **69**, 263 (1996).

[7] P. Schiffer, A.P. Ramirez, W. Bao and S. W. Cheong, Phys. Rev. Lett. **75**, 3336 (1995).

[8] R. von Helmolt, J. Wecker, B. Holzapfel, L. Schultz, K. Samwer, Phys. Rev. Lett. **71**, 2331 (1993).

[9] K. Chahara, T. Ohno, M. Kasai, and Y. Kozono, Appl. Phys. Lett. **63**, 1990 (1993).

[10] S. Jin, H. M. O'Bryan, T. H. Tiefel, M. McCormack, and W. W. Rhodes, Appl. Phys. Lett. 66, 382 (1995).

[11] H. Y. Hwang, S. W. Cheong, P. G. Radaelli, M. Marezio, and B. Batlogg, Phys. Rev. Lett. **75**, 914 (1995).

[12] J. Z. Sun, L. Krusin-Elbaum, S. S. P. Parkin and G. Xiao, Appl. Phys. Lett. **67**, 2726 (1995).

[13] Y. Tomika, A. Asamitsu, Y. Moritomo, H. Kuwahara, and Y. Tokura, Phys. Rev. Lett. **74**, 5108 (1995).

[14] S. Jin, T. H. Tiefel, M. McCormack, H. M. O'Bryan, L.H. Chen, R. Ramesh, and D. Schurig, Appl. Phys. Lett. **67**, 557 (1995).

[15] A. Gupta, T. R. McGuire, P. R. Duncombe, M. Rupp, J. Z. Sun, W. J. Gallagher, and G. Xiao, Appl. Phys. Lett. **67**, 3494 (1995).

[16] J.L. Simond, Physics Today, April 1995, p. 26.

[17] G.A. Prinz, Physics Today, April 1995, p. 58.

[18] J. Z. Sun, L. Krusin-Elbaum, P. R. Duncome, A. Gupta and R. B. Laibowitz, Appl. Phys. Lett. (in press)

[19] G. H. Jonker and J. H. van Santen, Physica **16**, 337 (1950).

[20] E. O. Wollan and W. C. Koehler, Phys. Rev. **100**, 545 (1955).

[21] P. G. deGennes, Phys. Rev. **118**, 141(1960).

[22] J. B. Goodenough, Phys. Rev. **100**, 564 (1955).

[23] B. C. Tofield and W. R. Scott, J. Solid State Chem. **10**, 183 (1974).

[24] C. W. Searle and S. T. Wang, Canadian J. Phys. **48**, 2023 (1970).

[25] C. Zener, Phys. Rev. **82**, 403 (1951).

[26] J.B. Goodenough, in Progress in Solid State Chemistry, edited by H. Reiss (Pergamon, New York, 1971), vol. 5, chap. 4, p. 325.

[27] R. M. Kusters, J. Singleton, D. A. Keen, R. McGreevy, and W. Hayes, Physica B**155**, 362 (1989).

[28] L. K. Leung, A. H. Morrish, and C. W. Searle, Can J. Physics **47**, 2697 (1969).

[29] S. S. P. Parkin, R. Bhadra, and K. P. Roche, Phys. Rev. Lett **66**, 2152 (1991).

[30] B. Dieny, P. Humbert, V. S. Speriosu, S. Metin, B. A. Gurney, P. Baumgart, and H. Lefakis, Phys. Rev. B**45**, 806 (1992).

[31] E. E. Fullerton, M. J. Conover, J. E. Mattson, C. H. Sowers, and S. D. Bader, Appl. Phys. Lett. **63**, 1699 (1993).

[32] L. H. Chen, T. H. Tiefel, S. Jin, R. B. van Dover, E. M.

Gyorgy, and R. M. Fleming, Appl. Phys. Lett. **63**, 1279 (1993).

[33] A. E. Berkowitz, J. R. Mitchell, M. J. Carey, A. P. Young, S. Zhang, F. E. Spada, F. T. Parker, A. Hutten, and G. Thomas, Phys. Rev. Lett. **68**, 3744 (1992).

[34] P. M. Levy, Science **265**, 972 (1992).

[35] T. L. Hylton, K. R. Coffey, M. A. Parker, and J. K. Howard, Science **261**, 1021 (1993).

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