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Dilution of two-dimensional antiferromagnetism by Mn site substitution in $La_1Sr_2Mn_{2-x}Al_xO_7$

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We report the effect of Al substitution on the Mn site of the bilayered half doped manganite $La_1Sr_2Mn_2O_7$. This substitution dilutes the magnetically active Mn-O-Mn network without introducing an appreciable distortion in the lattice, and ionic considerations lead to a predominant reduction of Mn^{4+} with increasing Al. The rate of fall of the long-range antiferromagnetic transition temperature as a function of substitution is seen to match well with established quasi-two-dimensional (quasi-2D) Heisenberg systems indicating that the nature of magnetic interactions in this quasi-2D system is of the short-range Heisenberg type. The magnetic contribution of the specific heat estimated using Fisher's relation could be fitted with a function incorporating the presence of a gapped Fermi surface appropriate for this type of system. The resistivity is seen to increase as a function of substitution due to the weakening of the double exchange within the ferromagnetic layers of this *A*-type of antiferromagnets and justifiably, in the paramagnetic region the data could be fitted to Mott's equation for the variable range hopping of polarons in two dimensions.

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I. INTRODUCTION

Mn-based Ruddlesden-Popper[1] compounds $(LaSr)_{n+1}Mn_nO_{3n+1}$ are known to have a layered structure in which n-MnO_3 blocks are separated by an additional $(La_{1-x}Sr_x)O$ layer. The perovskite structure corresponds to the $n=\infty$ and the K_2NiF_4 structure to $n=1$ members of this series. The bilayered $(n=2)$ manganites $La_{2-2x}Sr_{1+2x}Mn_2O_7$ have been extensively investigated ever since the $x=40\%$ member of this series showed collosal magnetoresistance,[2] albeit at lower temperatures. The structural consequence of moving from the perovskite $(n=\infty)$ to the bilayer $(n=2)$ is the introduction of a two-dimensional (2D) character to the system. The number of next neighbor Mn cations around each transition metal site reduces from six to five, thus providing an anisotropic reduction in the one-electron (e_g) bandwidth, as a consequence of which the electronic and transport properties are interestingly modified.

One of the most intriguing phenomena observed in perovskite manganites is the real-space ordering of Mn^{3+} and Mn^{4+} ions. This *charge ordering*[3] (CO) is frequently observed at commensurate compositions, provided the bandwidth (W) is not large. In the vicinity of 50% hole doping, a variety of perovskite manganites show the so-called charge-exchange (CE)-type of spin ordering, which is made up of zig-zag ferromagnetic chains ordered antiferromagnetically.[4] In analogy with the three-dimensional (3D) manganites, the bilayered manganite $La_1Sr_2Mn_2O_7$ is also expected to show similar spin/charge ordering considering the fact that it has an equal amount (50%) of Mn^{3+} and Mn^{4+} ions. Though initial diffraction experiments supported this point of view,[5] later results have indicated that the CE-type of spin/charge ordering exists only at intermediate temperatures[6] and that its volume fraction is small as compared to the much more dominant *A*-type of antiferromagnetic (AFM) state.[7]

Mn site substitution is now emerging as an interesting route in the study of mixed valent manganites in general, and charge and orbital ordered compositions in particular. This method involves the substitution of a magnetic or nonmagnetic element in the Mn site, thus disturbing or diluting the Mn-O-Mn network. Since the transport and magnetism in this class of compounds are dictated by the interactions within the Mn-O-Mn network, any substitution into this network drastically modifies the physical properties. Since the charge and orbital ordered manganites are of current interest, it is not surprising that a variety of Mn site substitutions on these compounds specially concentrating in the half-doped regions are now being reported.[8] The physical properties induced as a function of impurity substitution in half-doped manganites are known to depend crucially on both the nature of magnetic ordering of the parent compound (*A* or CE-type) as well as on the electronic configuration (magnetic or nonmagnetic) of the impurity used.

For example, in perovskite systems with a narrow bandwidth exhibiting the CE-type of antiferromagnetic ordering, the introduction of magnetic Cr impurities is known to destabilize the antiferromagnetic ground state into a low-temperature ferromagnetic one at relatively small (approx 3%) impurity substitution.[9] In this case, the long-range charge ordering is seen to collapse into a short-range one with correlation lengths of the order of 100 Å. Interestingly, the collapse of the CO is seen to be relatively independent of the nature (magnetic or nonmagnetic) of the impurity used, as seen in samples with Cr (d^3) and Sc (d^0) doping, indicating that it is primarily a manifestation of the disorder introduced in the magnetic lattice. The introduction of nonmagnetic Al (d^0) impurities in systems with CE-type of AFM ordering is shown to suppress the AFM transition temperature and exhibit finite-size effects in certain compositions.[10]

On the other hand, in relatively larger bandwidth systems (with the layered *A*-type of AFM ordering), the introduction of magnetic Cr impurities is not seen to result in the formation of a ferromagnetic ground state and long-range AFM order is seen to persist much above 5% of impurity substitution.[9] As far as nonmagnetic impurities are concerned, doping of trivalent elements (Al, Ga, In) is seen to cause an enhancement of the AFM transition temperature, whereas doping of tetravalent elements (Ti, Sn) is seen to suppress the AFM state.[11] Here, it is interesting to note that the *A*-type of AFM ordering persists, even in the presence of impurities, and the evolution of a ferromagnetic ground state is not usually seen.

The current consensus is that in CE systems, impurities with partially filled *d* bands cause a broadening of the e_g bandwidth as a consequence of which metallicity and ferromagnetism are induced.[12] The most popular magnetic dopants to date have been Cr^{3+} and Fe^{3+}. Cr^{3+}, by virtue of its electronic configuration of $t_{2g}^3\, e_g^0$ (isoelectronic with Mn^{4+}), is known to form ferromagnetic microdomains in the charge ordered matrix, presumably arising from the quenched random field arising from the Cr impurities.[13] Upon only a few percent of Cr substitution, percolation of these ferromagnetic clusters is known to result in a metal-insulator transition, even in the absence of a magnetic field, and the volume fraction of the ferromagnetic phase can be tailored as a function of either the Cr content, or the applied field. In a system with *A*-type of antiferromagnetic ordering, introduction of Cr impurities is observed to lead to a low-temperature reentrant spin-glass phase at low doping concentrations, presumably arising as a consequence of competing interactions between the AFM order and the ferromagnetism induced as a function of Cr substitution.[14] On the contrary, Fe^{3+}, due to its filled e_g orbitals, disrupts the double exchange interaction[15] and there is evidence to show that the doped Fe couples antiferromagnetically to the host Mn lattice.[16] Thus, it is not surprising that a variety of effects commensurate with a magnetically phase-separated state is observed in such systems.[17]

As far as nonmagnetic impurities are concerned, one would expect impurities with fully filled (or empty) *d* bands to dilute the Mn-O-Mn network without introducing any magnetic interactions of its own. However, in these cases, disorder induced by ionic size mismatch can lead to structural distortions accompanied by changes in the Mn-O bond lengths and Mn-O-Mn bond angles. Thus, apart from diluting the Mn-O-Mn network, such substitutions with appreciable ionic size mismatch leads to changes in the magnetic ground states. As mentioned earlier, in the half-doped charge ordered systems, such disorder is known to result in the collapse of the long-range charge ordering into a short-range ordered state with correlation lengths of the order of 100 Å.[9] Also, when substitutions are introduced into the half-doped parent composition, the Mn^{3+}/Mn^{4+} ratios would deviate away from unity, thus affecting the physical properties as dictated by both the phase diagram of the parent series as well as the nature (and ionic radii) of the impurity used.[18] Recent reports of a variety of field-induced metamagnetic effects in Mn site substituted manganites[19] has added to the interest in this class of materials. Though this avenue of research in half-doped three-dimensional (3D) perovskites has gained popularity in recent times, Mn site substitution in the layered (2D) analogs has not been adequately explored. Here, we report the structural, magnetic, and transport properties of a bilayered manganite series, where Al is substituted in the Mn site of the half-doped $La_1Sr_2Mn_2O_7$. Al was selected as a dopant on ionic considerations, as its ionic radii matches very well with that of Mn^{4+}.[20] Thus, one would expect minimal lattice distortion along with a preferential replacement of Mn^{4+}. Most importantly, Al with an empty *d* shell is nonmagnetic, and hence a simple dilution of the magnetic lattice would be expected.

TABLE I. Structural and fitting parameters determined from the Rietveld profile refinement of the powder XRD patterns for the series $La_1Sr_2Mn_{2-x}Al_xO_{7+\delta}$. Here, O1 refers to the apical oxygen in the double perovskite slab, O2 is the equitorial oxygen which lies in the plane of the perovskite layer, and O3 is the apical oxygen in the rocksalt layer. The mean valence state of Mn was determined by redox iodometric titrations.

Al (x)	0%	2.5%	5%	7.5%	10%
a(Å)	3.8707	3.8690	3.8652	3.8618	3.8544
c(Å)	19.9771	19.9820	19.9921	19.9982	20.0006
V(Å^3)	299.30	299.11	298.68	298.24	297.14
Mn-O1(Å)	1.949	1.958	1.969	1.976	1.984
Mn-O2(Å)	1.951	1.949	1.947	1.946	1.943
Mn-O3(Å)	1.962	1.966	1.982	1.998	2.032
Mn-O2-Mn	165.41°	165.51°	165.66°	165.82°	165.98°
Mn^{3+}%	49.0	48.5	47.6	46.7	45.7
Mn^{4+}%	51.0	49.0	47.4	45.8	44.3

II. SAMPLE PREPARATION AND CHARACTERIZATION

Polycrystalline samples of $La_1Sr_2Mn_{2-x}Al_xO_7$ ($0 \leqslant x \leqslant 10\%$) have been prepared using the standard solid-state ceramic route, with starting materials La_2O_3, $SrCO_3$, MnO_2, and Al_2O_3 of at least 99.99% purity. The powdered samples are mixed and initially treated at 1000 °C for 24 h after which they are pelletized, reground, and treated at 1250 °C (24 h) and 1500 °C (36 h) with intermediate grindings. X-ray diffraction (XRD) is done using a Rigaku Rotaflex RTC 300RC powder diffractometer with Cu $K\alpha$ radiation. All the samples are seen to crystallize in the tetragonal (I4/mmm) structure. Rietveld profile refinement[21] of powder XRD data is used to determine the structural parameters tabulated in Table I. As is clearly seen, the variation in the structural parameters is $<1\%$ indicating that Al doping does not introduce any major structural distortion. The values of the mean Mn valence determined by using iodometric redox titrations (using sodium thiosulphate and potassium iodide) unambiguously indicate a preferential replacement of Mn^{4+} with increasing Al substitution. The presence of stacking faults in the double layered structure is known to result in the formation of parasitic $(LaSr)MnO_3$ and $(LaSr)_2MnO_4$ phases.[22] A parasitic perovskite phase has been detected in our samples and (using Rietveld profile refinement) is estimated to make up $\approx 3\%$ of the volume fraction. However, we have reasons to believe that the presence of this intergrowth does not adversely affect the nature of magnetism and transport in these samples, at least in the temperature ranges of our interest.

III. RESULTS AND DISCUSSIONS

A. ac susceptibility

Magnetic susceptibility measurements are done using a homemade ac susceptometer.[23] The parent compound

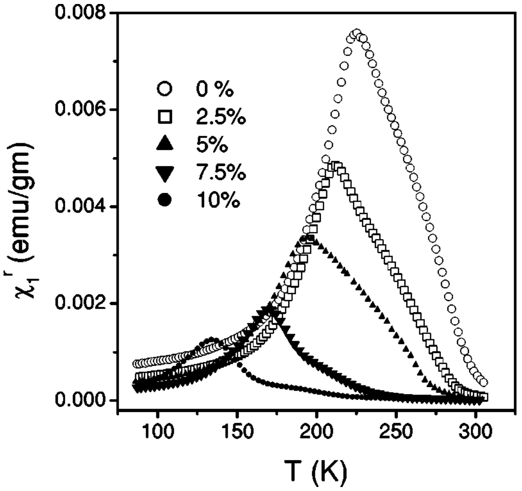

FIG. 1. The real part of first-order ac susceptibility plotted as a function of temperature for the series $La_1Sr_2Mn_{2-x}Al_xO_7$. The transition temperatures are seen to shift to lower temperatures with increasing Al doping.

$La_1Sr_2Mn_2O_7$ is known to order antiferromagnetically at ≈ 225 K and since Al substitution dilutes the magnetically active Mn-O-Mn network, one would expect the transition temperatures to drop to lower temperatures with increasing Al substitution. This is clearly seen in Fig. 1, where the temperature dependence of the real part of ac susceptibility for the whole series shows a rapid reduction of the Neel temperature (T_N) as a function of increasing Al doping.

This problem of site dilution has been extensively studied in the past in an attempt to understand the nature of percolation in magnetic systems and the rate of fall in T_N is known to depend on the universality class to which the system belongs. For instance, according to the mean-field theory, the long-range T_N decreases linearly with increasing nonmagnetic substitution and long-range order disappears only when all the magnetic ions are substituted by nonmagnetic ones. For quasi-2D Ising systems (like $K_2Co_2F_4$, see Ref. 24), this drop is known to be much more rapid and long-range order disappears at a dopant concentration of $x \approx 40\%$, which is the site percolation threshold for a 2D lattice. However, for systems like $La_2Cu_{1-x}Mg_xO_4$,[25] which are known to be 2D Heisenberg-like, the fall in T_N is even more drastic and long-range order is expected to disappear at $x \approx 20\%-25\%$. A useful parameter for the comparison of various systems is the initial suppression rate (R_{IS}) defined as $-\partial[T_N(x)/T_N(0)]/\partial x$. For our system, we obtain $R_{IS} \approx 2.7$, which is close to that of other 2D Heisenberg systems.[25] This is shown in Fig. 2, where the fall in T_N is shown as a function of substitution. Our data is seen to match very well with that of $La_2Cu_{1-x}Mg_xO_4$, a well-established 2D Heisenberg system. *Thus our results clearly indicate that the nature of magnetic interactions in this bilayered series are of the short-range 2D Heisenberg type*. However, rigorous measurements of the critical region can be made to reconfirm this observation. This is a systematic study of a manganite system, where the effects of site dilution have been used to determine the nature of magnetic interactions.

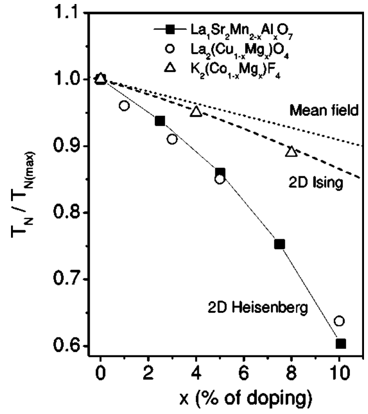

FIG. 2. The normalized Neel temperatures $[T_N/T_{N(\max)}]$ plotted as a function of substitution for various quasi-2D systems. The data for $K_2(Co_{1-x}Mg_x)F_4$ and $La_2(Cu_{1-x}Mg_x)O_4$ are from Refs. 24 and 25, respectively. The skewed lines are guides to the eye indicating the effect of site dilution on a mean field and Ising square lattice system.

B. Magnetic contribution to specific heat

Accurate determination of the magnetic contribution to the specific heat is a nontrivial exercise, due to the fact that total subtraction of the electronic and lattice contributions from the measured specific heat is not straightforward. However, a useful estimation, at least of its functional form, can be made using the Fisher's relation,[26] which by the use of general thermodynamic considerations relates the magnetic contribution of the specific heat with the measured susceptibility across a para-antiferromagnetic transition. This relation is expected to be valid in the transition region lying above $0.5T_N$, where effects of additional contributions like the anisotropy, coupling between more distant neighbors, etc., which have been excluded from the original derivation,[26] are only expected to yield a slowly varying contribution to the mean magnetic energy. The experimental verification of Fisher's relation has been conclusively shown[27] and it is an established technique in investigating antiferromagnetic transitions.[28] Fisher's relation states that in a paramagnetic-antiferromagnetic transition, the magnetic contribution to the specific heat (C_{mag}) mirrors the behavior of $\partial(\chi T)/\partial T$; i.e., $C_{mag} = \alpha \partial(\chi T)/\partial T$, where α is a relatively slowly varying function of temperature. Figure 3 shows the temperature dependence of $\partial(\chi T)/\partial T$ for the whole series. All the samples show a typical λ-type feature, which is a signature of an antiferromagnetic transition. The temperature of the peak of this feature is marginally smaller than the temperature where the peak in susceptibility occurs, as is expected in layered systems, where the effect of short-range (2D) correlations are known to be more pronounced.[29] The data close to the transition region for $T < T_N$ could be fitted to an equation,

$$\partial(\chi T)/\partial T \propto C_{mag} = \alpha \exp(-\Delta/T),$$

where the $\exp(-\Delta/T)$ term arises from the presence of a gapped Fermi surface.[30] In the temperature range of our interest ($[T/T_N] \approx 0.67$), which is smaller than the range prescribed by Fisher ($[T/T_N] \approx 0.5$) the constant of proportion-

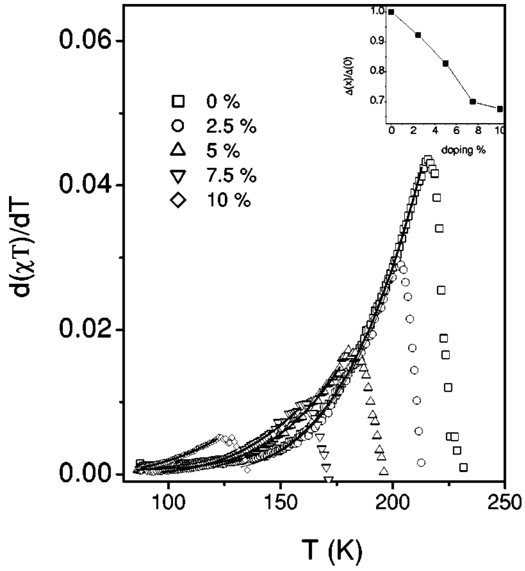

FIG. 3. The magnetic contribution to the specific heat plotted as a function of temperature for the series $La_1Sr_2Mn_{2-x}Al_xO_7$. The solid line indicates fits incorporating the presence of a gapped Fermi surface. The inset shows the normalized value of Δ plotted as a function of the dopant concentration.

ality in the Fisher's relation (α) can be considered to be relatively independent of T, as its variation is expected to be within 10% of its value at T_N.[26] Good fits could be obtained for all the samples in the range up to $[T/T_N] \approx 0.67$, and the magnitude of Δ was seen to reduce with increasing Al doping as is shown in the inset of Fig. 3. The fact that a satisfactory fit could be obtained using a single T-dependent fitting function not only indicates that the range of fitting is reasonable, but also validiates the functional form of the fitting as well. Moreover, we have determined the range of fitting by monitoring the error of fitting σ^2, where σ is the root-mean-square deviation of the fitted and measured data. The data below $[T/T_N] \approx 0.67$ could be fitted incorporating an additional term (T^3) arising due to the presence of antiferromagnetic spin waves (magnons).[32] However, we have refrained from including it in our analysis, considering the fact that the constant of proportionality used in the Fisher's relation can be considered to be independent of T only *in the vicinity* of the transition, and hence fitting the data far away from this region could result in considerably larger errors.

Since we are dealing with the analysis of bulk magnetic susceptibility data, the gap which is seen in our fitting procedure is essentially a gap in the magnon spectra, which is seen in many antiferromagnetic systems. However, the origin of the gap (Δ) used in fitting our data is not easy to discern. Possible mechanisms that can be considered include the effect of spin, charge or orbital order, a Coulomb gap, strong electron-lattice coupling, or even a simple splitting of the levels due to the Jahn-Teller effect on the Mn^{3+} ions. It would be unrealistic to accurately determine the origin of this gap, at least on the basis of an analysis of bulk magnetization data. It is to be noted that the presence of a *pseudogap* has been shown in a layered system $La_{1.2}Sr_{1.8}Mn_2O_7$ using angle-resolved photoelectron spectroscopy (ARPES), where it was clearly shown that the spectral weight at the Fermi level (E_F) was severely depressed in the low-temperature phase.[31] In comparison to the perovskite compounds, in layered manganites, this pseudogap is probably stronger because of the narrower electron bandwidth arising due to the reduced dimensionality. The values of these gaps, as determined by our fitting procedure, are seen to systematically vary from 113 to 76.3 meV as one increases the percentage of Al substitution, clearly indicating a softening of the gap with increasing dilution of the magnetic lattice. The value of this gap in the magnon spectrum with respect to its transition temperature ($\approx 6-7$ times T_N) is reasonable and similar to that in a charge-density wave system URu_2Si_2, where a gap of ≈ 7 times T_N was deduced from specific heat measurements. However, in the system NaV_2O_5, heat capacity measurements have indicated a gap of ≈ 3.5 times T_N.[33] It should be borne in mind that systems like this series under consideration may have a larger gap in the magnon spectra as a result of its inherently layered nature. Since we are not aware of any estimation of the spin gap in layered manganite systems, further scattering experiments would be needed to corroborate these values.

C. dc resistivity

Determination of the nature of electronic transport in hole-doped manganites is a problem that continues to elude solutions.[34] The current consensus is that the conduction, at least in the paramagnetic regime, occurs through the hopping of charged carriers localized in the form of polarons. These polarons could be *dielectric* polarons, where the electron bears with it a dilation of the MnO_6 octahedron, or a *Jahn-Teller* polaron, due to the axial distortion of the octahedron. The paramagnetic state of the layered manganites has received much lesser attention, though early studies on $La_{1.2}Sr_{1.8}Mn_2O_7$ drastically demonstrated the effect of dimensionality, as the conduction along the *ab* plane indicated the presence of *Zener-pair* polarons, whereas along the *c* axis adiabatic small polaronic behavior was concluded.[35] Recently, the conduction in the paramagnetic state of $La_1Sr_2Mn_2O_7$ was reported to be due to the variable range hopping (VRH) of polarons in the presence of a Coulomb gap.[36] In general, Mott's VRH[37] is described by $\rho = \rho_0 \exp[T_0/T]^p$, where $p = 1/(d+1)$ with "d" being the dimensionality of the system. Mott's activation energy (T_0) $\propto 1/N(E)\xi^d$, where $N(E)$ is the density of states at the Fermi level and ξ is the localization length. However, in our case the transport data in the paramagnetic region of all the samples is seen to have a much better fit to Mott's equation for VRH in two dimensions ($p = 1/3$) than to a VRH in the presence of a Coulomb gap ($p = 1/2$) as is seen in Fig. 4. The values of T_0 were seen to increase with increasing Al doping, implying a decrease in the localization length, provided the density of states at the Fermi level does not change.

The transport data in the region $T < T_N$ for all the samples is shown in Fig. 5, where the resistivity is seen to increase with increasing Al doping. This could be understood to be due to the destabilization of the A-type of the AFM state. This A-type of AFM is known to occur in systems with a

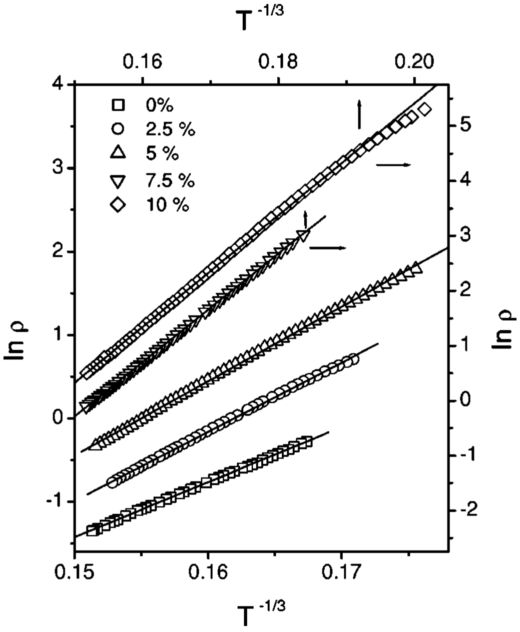

FIG. 4. Semilog plot of the resistivity (ρ) vs $T^{-1/3}$ of $La_1Sr_2Mn_{2-x}Al_xO_7$ for $T > T_N$. The lines are linear fits to the experimental data indicating that the 2D variable range hopping mechanism is valid in the paramagnetic region.

relatively large bandwidth[38] and is of a 2D character, where the e_g electrons in each *ab* (ferromagnetic) plane are itenerant. Here, the e_g electrons supposedly occupy the isotropic (and delocalized) $d(x^2-y^2)$ orbitals,[39] in contrast to the CE-type of half-doped AFMs, where the e_g electrons occupy the anisotropic (and localized) $d(3x^2-r^2)$ and $d(3y^2-r^2)$ orbitals alternately.[40] These ferromagnetic layers are then aligned antiferromagnetically, making up this anisotropic antiferromagnet. Al substitution randomly cuts the electronically and magnetically active Mn-O-Mn network and reduces the effective double exchange strength within these ferromagnetic layers, resulting in a net increase in the resistivity. This behavior is at variance with that seen in a 3D perovskite charge ordered system, $Pr_{0.5}Ca_{0.5}MnO_3$, with a CE-type of AFM ordering, where Al substitution was seen to reduce the value of the resistivity in the (weakened) charge ordered region.[10] *This clearly brings forward the contrasting effects that nonmagnetic substitution has on half-doped manganites with different (i.e., A- or CE-type) antiferromagnetic ground states.*

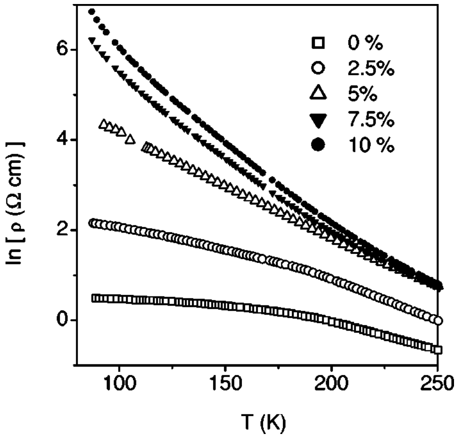

FIG. 5. Semilog plot of the resistivity (ρ) as a function of temperature for the series $La_1Sr_2Mn_{2-x}Al_xO_7$, clearly indicating the increase in resistivity as a function of Al doping. This arises due to the weakening of the double exchange within the ferromagnetic layers in these *A*-type antiferromagnets.

IV. CONCLUSIONS

In summary, the physical properties of a series of bilayered manganites is presented. Polycrystalline samples of Al substituted $La_1Sr_2Mn_2O_7$ were prepared to study the effect of nonmagnetic substitution in the half-doped bilayered manganites. The reduction in the values of T_N with increasing substitution was observed to be similar to that observed in a well-established 2D Heisenberg system, $La_2Cu_{1-x}Mg_xO_4$. This observation clearly indicates that the magnetic interactions in these bilayered systems are of the 2D Heisenberg-type. The magnetic contribution to the specific heat near the transition temperature estimated using Fisher's relation could be fitted to a term corresponding to a gapped Fermi surface, the magnitude of which was seen to decrease with increasing substitution. The resistivity of the samples was seen to increase in the region $T < T_N$ with increasing Al substitution, due to the reduction of the effective double exchange interaction within each layer of the *A*-type AFM, whereas in the paramagnetic region the conduction was seen to be of a simple 2D VRH form without a Coulomb gap.

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[1] S. N. Ruddlesden and P. Popper, Acta Crystallogr. **11**, 541 (1958).
[2] Y. Moritomo, A. Asamitsu, H. Kuwahara, and Y. Tokura, Nature (London) **380**, 141 (1996).
[3] *Colossal Magnetoresistance, Charge Ordering and Related Properties of Manganese Oxides*, edited by C. N. R. Rao and B. Raveau (World Scientific, Singapore, 1998).
[4] J. B. Goodenough, Phys. Rev. **100**, 564 (1955).
[5] J. Q. Li, Y. Matsui, T. Kimura, and Y. Tokura, Phys. Rev. B **57**, R3205 (1998).
[6] Tapan Chatterji, G. J. Mc'Intyre, W. Caliebe, R. Suryanarayanan, G. Dhalenne, and A. Revcolevschi, Phys. Rev. B **61**, 570 (2000).
[7] M. Kubota, H. Yoshizawa, Y. Moritomo, H. Fujioka, K. Hirota, and Y. Endoh, J. Phys. Soc. Jpn. **68**, 2202 (1999).
[8] V. Hardy, A. Maignan, S. Hebert, and C. Martin, Phys. Rev. B **67**, 024401 (2003); A. Maignan, V. Hardy, C. Martin, S. Hebert, and B. Reveau, J. Appl. Phys. **93**, 7361 (2003).

[9] T. Katsufuji, S.-W. Cheong, S. Mori, and C.-H. Chen, J. Phys. Soc. Jpn. **68**, 1090 (1999).

[10] S. Nair and A. Banerjee, cond-mat/0309406; Phys. Rev. Lett. **93**, 117204 (2004).

[11] B. Raveau, A. Maignan, C. Martin, and H. Hervieu, in *Colossal Magnetoresistance, Charge Ordering and Related Properties of Manganese Oxides*, edited by C. N. Rao and B. Raveau (World Scientific, Singapore, 1998).

[12] S. Hebert, A. Maignan, C. Martin, and B. Raveau, Solid State Commun. **121**, 229 (2002), and references therein.

[13] T. Kimura, Y. Tomioka, R. Kumai, Y. Okimoto, and Y. Tokura, Phys. Rev. Lett. **83**, 3940 (1999).

[14] J. Dho, W. S. Kim, and N. H. Hur, Phys. Rev. Lett. **89**, 027202 (2002).

[15] K. H. Ahn, X. W. Wu, K. Liu, and C. L. Chien, J. Appl. Phys. **81**, 5505 (1997).

[16] A. Simopoulos, M. Pissas, G. Kallias, E. Devlin, N. Moutis, I. Panagiotopoulos, D. Niarchos, C. Christides, and R. Sonntag, Phys. Rev. B **59**, 1263 (1999).

[17] P. Levy, F. Parisi, L. Granja, E. Indelicato, and G. Polla, Phys. Rev. Lett. **89**, 137001 (2002).

[18] P. V. Vanitha, Solid State Commun. **123**, 129 (2002).

[19] V. Hardy, A. Maignan, S. Hebert, C. Yaicle, C. Martin, M. Hervieu, M. R. Lees, G. Rowlands, D. Mc K. Paul, and B. Raveau, Phys. Rev. B **68**, 220402(R) (2003).

[20] R. D. Shannon and C. T. Prewitt, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **25**, 925 (1969).

[21] R. A. Young, A. Sakthivel, T. S. Moss, and C. O. Paiva-Santos, *Users Guide to Program DBWS-9411* (Georgia Institute of Technology, Atlanta, 1994).

[22] S. D. Bader, R. M. Osgood III, D. J. Miller, J. F. Mitchell, and J. S. Jiang, J. Appl. Phys. **83**, 6385 (1998).

[23] A. Bajpai and A. Banerjee, Rev. Sci. Instrum. **68**, 4075 (1997).

[24] D. J. Breed, K. Gilijamse, J. W. E. Sterkenburg, and A. R. Miedema, J. Appl. Phys. **41**, 1267 (1970).

[25] S.-W. Cheong, A. S. Cooper, L. W. Rupp, Jr., B. Batlogg, J. D. Thompson, and Z. Fisk, Phys. Rev. B **44**, 9739 (1991).

[26] M. E. Fisher, Philos. Mag. **7**, 1731 (1962).

[27] J. Skalyo, Jr., A. F. Cohen, S. A. Friedberg, and R. B. Griffiths, Phys. Rev. **164**, 705 (1967).

[28] Richard L. Carlin, *Magnetochemistry* (Springer-Verlag, Berlin, 1986).

[29] D. N. Argyriou, J. F. Mitchell, C. D. Potter, S. D. Bader, R. Kleb, and J. D. Jorgensen, Phys. Rev. B **55**, R11965 (1997).

[30] M. B. Maple, J. W. Chen, Y. Dalichaouch, T. Kohara, C. Rossel, M. S. Torikachvili, M. W. McElfresh, and J. D. Thompson, Phys. Rev. Lett. **56**, 185 (1986).

[31] D. S. Dessau, T. Saitoh, C.-H. Park, Z.-X. Shen, P. Villella, N. Hamada, Y. Moritomo, and Y. Tokura, Phys. Rev. Lett. **81**, 192 (1998).

[32] E. S. R. Gopal, *Specific Heats at Low Temperatures* (Plenum, New York, 1966).

[33] A. N. Vasil'ev, M. M. Markina, M. Yu. Kagan, M. Isobe, and Y. Ueda, Pis'ma Zh. Eksp. Teor. Fiz. **73**, 401 (2001) [JETP Lett. **73**, 357 (2001)].

[34] M. B. Salamon and M. Jaime, Rev. Mod. Phys. **73**, 583 (2001).

[35] J. S. Zhou, J. B. Goodenough, and J. F. Mitchell, Phys. Rev. B **58**, R579 (1998).

[36] X. J. Chen, C. L. Zhang, J. S. Gardner, J. L. Sarrao, and C. C. Almasan, Phys. Rev. B **68**, 064405 (2003).

[37] N. F. Mott and E. A. Davies, *Electronic Processes in Noncrystalline Solids*, 2nd ed. (Clarendon, Oxford, 1979).

[38] H. Kawano, R. Kajimoto, H. Yoshizawa, Y. Tomioka, H. Kuwahara, and Y. Tokura, Phys. Rev. Lett. **78**, 4253 (1997).

[39] K. Hirota, Y. Moritomo, H. Fujioka, M. Kubota, H. Yoshizawa, and Y. Endoh, J. Phys. Soc. Jpn. **67**, 3380 (1998).

[40] Y. Murakami, H. Kawada, H. Kawata, M. Tanaka, T. Arima, Y. Moritomo, and Y. Tokura, Phys. Rev. Lett. **80**, 1932 (1998).