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Cooperative Jahn-Teller effect and electron-phonon coupling in La$_{1-x}A_x$MnO$_3$

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A classical model for the lattice distortions of La$_{1-x}A_x$MnO$_3$ is derived and, in a mean field approximation, solved. The model is based on previous work by Kanamori and involves localized Mn *d* electrons (which induce tetragonal distortions of the oxygen octahedra surrounding the Mn) and localized holes (which induce breathing distortions). Parameters are determined by fitting to the room temperature structure of LaMnO$_3$. The energy gained by formation of a local lattice distortion is found to be large, most likely ≈ 0.6 eV per site, implying a strong electorn-phonon coupling and supporting polaronic models of transport in the doped materials. The structural transition is shown to be of the order-disorder type; the rapid *x* dependence of the transition temperature is argued to occur because added holes produce a ''random'' field which misaligns the nearby sites.

I. INTRODUCTION

LaMnO$_3$ is an insulator which undergoes a structural phase transition at a $T_s(x=0) \sim 750$ K. The high-temperature phase is believed to be cubic. The low-temperature phase is approximately tetragonal, with one lattice constant about 0.15 Å shorter than the other two.[1] Several other rather small-amplitude (~ 0.01 Å) distortions also occur at temperatures less than or equal to T_s,[2] and the structure at room temperature is orthorhombic. These small distortions will be ignored here. As the composition is varied to La$_{1-x}A_x$MnO$_3$, there are two changes. First, $T_s(x)$ decreases rapidly and vanishes at $x = x_s \approx 0.2$.[1,2] Second, the resistivity decreases.[3] However, for $x < x_{\mathrm{cond}} \approx 0.3$ and temperatures of order room temperature and higher, the material is still insulating in the sense that the resistivity is much higher than the Mott limit, and increases as T is decreased.[4] In this regime a description of the resistivity in terms of classical particles hopping on a lattice has been shown to be self-consistent.[5]

This paper presents a model for the $x < x_{\mathrm{cond}}$ regime and an explanation for the x dependence of T_s. The physical picture is as follows: The electrically active orbitals are believed to be the Mn $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ orbitals. The mean occupancy is $1-x$.[1,6] Because the conductivity is so low, the electrons are treated classically. It is assumed that a site is occupied, with probability $1-x$ or empty, with probability x. The d orbitals are degenerate if the local environment has cubic symmetry; the degeneracy is lifted by a tetragonal distortion of the local environment. Kanamori[7] deduced that at $x=0$ the primary lattice distortion occurring at T_s is a staggered (π,π,π) tetragonal distortion of the oxygen octahedra surrounding the Mn sites, driven by a Jahn-Teller splitting of the outer Mn d levels; anharmonic terms in the elastic energy couple this to the uniform strain, producing the lattice parameter changes observed in early scattering experiments. Kanamori's deduction was subsequently confirmed by more detailed studies of the structure.[2] In this paper ionic displacements will be explicitly included in Kanamori's model, a fit to data will be given, and the model will be extended to $x > 0$. It will be shown that the energies involved in the Jahn-Teller physics are much larger than any relevant temperature, so that as long as a classical picture for the electrons is appropriate, a local tetragonal distortion will occur around each Mn site where there is an outer shell electron. At each unoccupied site a breathing mode distortion will occur; this will act as an effective random field on the staggered tetragonal distortions, and will prevent them from ordering. If the tetragonal distortions are not coherent throughout the lattice, they cannot couple to the uniform strain, and the material will remain approximately cubic.

The model considered here is a version of the ''cooperative Jahn-Teller effect,'' which has generated an enormous literature.[8] Surprisingly, rather little attention has been paid to LaMnO$_3$ since the pioneering work of Kanamori. A Hamiltonian describing the orbital ordering of LaMnO$_3$ was derived from a purely electronic multiband Hubbard model by Kugel and Khomskii[9] and a similar Hamiltonian has recently been derived and studied via mean field theory by Ishihara *et al.*,[10] but atomic displacements and electron-phonon coupling have not been considered. The aspects of the present paper are the explicit inclusion of the lattice degrees of freedom, which allows values for the electron-phonon coupling in LaMnO$_3$ to be deduced from data, and the discussion of the ''random field'' effect of holes.

The rest of this paper is organized as follows. In Sec. II the model is derived. In Sec. III the parameters are determined by fitting structural data for LaMnO$_3$ to the model. In Sec. IV the effects of added holes are discussed. Section V is a conclusion. Technical details of calculations are given in several Appendices.

II. MODEL

In this section the energy functional is derived. The main physical assumption is that all degrees of freedom may be treated classically. The electrons are regarded as the fundamental degrees of freedom and are taken to be localized on lattice sites. In a classical model the hopping of electrons from site to site does not affect the energy, and so will be neglected. Note also that the physical mechanism primarily responsible for localization could be the electron-phonon coupling discussed here or the ''Hubbard-U'' effects considered by other authors.[11] The cause of the localization is not

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relevant to the considerations of this paper, and so the electronic correlation effects need not be explicitly considered.

For each fixed configuration of electrons, the phonon part of the free energy is minimized; the result of this minimization is the energy of that configuration of electrons. The phonons are treated in the harmonic approximation. The effect of the undoubtedly important anharmonic terms in the lattice energy is parametrized. Only some of the lattice degrees of freedom are considered. These are (1) the vector displacements $\vec{\delta}_i$ of the manganese (Mn) ion on site i and (2) the scalar displacement $u_i^{(a)}$ of the oxygen (O) ion along the Mn-O-Mn bond direction. Thus u_i^x is the displacement, in the x direction, of the O atom which sits between the Mn ion on site i and the Mn ion on site $i+\hat{x}$. With this restricted set of displacements one may discuss the Jahn-Teller distortion and the uniform strain, but not the buckling of the Mn-O-Mn bond or the associated rotation of the octahedra. These latter lattice distortions occur but, I believe, are not fundamental.

If an electron is present on site i, it will be in a state $|\psi_i(\theta)\rangle$ given by a linear combination of the two outer d orbitals. In the classical approximation used here the phase of the electron is of no significance, and so one may write

$$|\psi_i(\theta_i)\rangle = \cos\theta_i |d_{3z^2-r^2}\rangle + \sin\theta_i |d_{x^2-y^2}\rangle, \tag{1}$$

with $0 \leqslant \theta_i < \pi$.

The lattice energy E_{latt} is taken to depend on the Mn-O distance and the Mn-Mn distance. The unit cell i is taken to include the Mn ion at position $\vec{R}_i + b\vec{\delta}_i$ and the three O ions at positions $\vec{R}_i + (\frac{1}{2}b + bu_i^{(a)})\hat{a}$, where $a = x,\ y$, or z and b is the lattice constant. Here δ and u are dimensionless displacements defined with reference to the ideal perovskite lattice with lattice constant b. In the harmonic approximation

$$E_{\text{latt}} = \frac{1}{2}K_1 \sum_i \ (\delta_i^a - u_i^a)^2 + (\delta_i^a - u_{i-\hat{a}}^a)^2 + \frac{1}{2}K_2 \sum_i \ (\delta_i^a - \delta_{i-\hat{a}}^a)^2. \tag{2}$$

Here K_1 and K_2 have the dimension of energy; one expects $K_1 \geqslant K_2$.

If an electron is present on site i, there is an electron-lattice energy given by

$$E_{\text{JT}} = \lambda \sum_i \ (1-h_i)\left[\cos 2\theta_i \left(v_i^z - \frac{1}{2}(v_i^x + v_i^y) \right) + \sin 2\theta_i \frac{\sqrt{3}}{2}[v_i^x - v_i^y]\right]. \tag{3}$$

Here

$$v_i^a = u_i^a - u_{i-\hat{a}}^a \tag{4}$$

and $h_i = 0$ if an electron is present on site i and $h_i = 1$ if not. Finally, if there is no electron present on site i, all of the neighboring oxygen ions are equally attracted to it, leading to

$$E_{\text{hole}} = \beta\lambda \sum_i \ h_i[v_i^x + v_i^y + v_i^z]. \tag{5}$$

One expects $\beta \gg 1$ because the force exerted on the surrounding oxygen ions by a Mn of the wrong charge must be much greater than the force exerted by rearranging the proper charge among different d orbitals.

For fixed values of θ_i and h_i, Eqs. (2), (3), and (5) may be minimized. The details are given in Appendix A. The result is most naturally expressed in terms of the parameters

$$E^0 = -\frac{3}{2}\frac{\lambda^2}{K_1}\frac{K_1+K_2}{K_1+2K_2}, \qquad \kappa = \frac{1}{2}\frac{\lambda^2 K_2}{K_1(K_1+2K_2)}\,, \tag{6}$$

as

$$E = E^0 \sum_i \ (1-h_i)^2 + \beta^2 h_i^2 + A\cos 6\theta_i + \kappa \sum_{ia} \ (1-h_i)(1 - h_{i+\hat{a}})\cos 2(\theta_i + \psi_a)\cos 2(\theta_{i+a} + \psi_a) + 2\beta\kappa \sum_{ia} \ h_i(1 - h_{i+a})\cos 2(\theta_{i+a} + \psi_a) + \beta^2 \kappa \sum_{ia} \ h_i h_{i+a}\,. \tag{7}$$

Here $a = \pm x,y,z$, $\psi_{\pm z} = 0$, $\psi_{\pm x} = -\pi/3$, $\psi_{\pm y} = \pi/3$, and we have followed Kanamori[7] by adding a phenomenological anharmonicity term with coefficient A. Cubic anharmonicities exist in any realistic model of lattice dynamics. The anharmonicity is important for two reasons: it couples a staggered distortion to a uniform one, and it breaks the perfect rotational (θ) symmetry found otherwise if $h_i = 0$. The term added to Eq. (7) is the simplest one which accomplishes these two effects and goes into itself under $\theta \rightarrow \theta + \pi$ as required. It is derived in Appendix A.

To each configuration of orbital occupancies $\{\theta_i\}$ corresponds an average distortion from the ideal cubic peroviskite structure. This may be written in terms of the oxygen (u) and Mn (δ) displacements as

$$u_i^a = \sum_j \ \phi_u^a(R_i - R_j)[(1-h_j)\cos 2(\theta_j + \psi_j^a) + \beta h_j],$$

$$\delta_i^a = \sum_j \ \phi_\delta^a(R_i - R_j)[(1-h_j)\cos(2\theta_j + \psi_j^a) + \beta h_j]. \tag{8}$$

The elastic kernels are

$$\phi_u^a(R) = \frac{\lambda}{K_1}\sum_k \frac{e^{ik\cdot R}(1-e^{-ik_a})[K_1 + K_2(1-\cos k_a)]}{(K_1+2K_2)(1-\cos k_a)},$$

$$\phi_\delta^9(k) = \frac{\lambda}{K_1}\sum_k \frac{e^{ik\cdot R}K_1\cos(k_a/2)(1-e^{-ik_a})}{K_1 + K_2(1-\cos k_a)}. \tag{9}$$

III. FIT TO DATA

In this section the structural information of Ref. 2 is used to estimate model parameters. The analysis is essentially that of Kanamori.[7] A two-sublattice ordering of Jahn-Teller distortions parametrized by angles θ_1 and θ_2 is assumed. By fitting the observed atomic displacements to Eqs. (A2) and

TABLE I. Values of the parameters deduced by fitting mean-field theory to structural data.

K_2/K_1	$2\theta_1^{(0)}$	λ/K_1	$E_0/K_1\times10^3$	$\kappa/K_1\times10^4$	A/κ
0	80.9	0.044	2.9	0	0.70
0.1	79.2	0.045	2.8	0.85	0.87
0.3	75.7	0.045	2.5	1.9	1.31
0.5	72.3	0.046	2.4	2.6	1.92
0.75	68.2	0.047	2.4	3.4	3.31
1	64.4	0.049	2.4	4.0	6.93

(A7), θ_1,θ_2 and elastic constants are determined. By requiring that the deduced θ_1,θ_2 minimize Eq. (7) the anisotropy energy A is found. The experimental data for the structure are given in Appendix B and the mean field equations are solved in Appendix C.

It is convenient to express the lattice distortions in terms of a staggered oxygen displacement $\vec{u}_s$ and a uniform strain $\vec{e}$. By rewriting Eqs. (A2), (A7) we obtain

$$u_s^a=\frac{\lambda}{2K_1}[\cos2(\theta_1+\psi^a)-\cos2(\theta_2+\psi^a)],$$

$$e^a=\frac{2\lambda}{(K_1+2K_2)}\{\cos2(\theta_1+\psi^a)+\cos2(\theta_2+\psi^a)\}. \tag{10}$$

In Appendix B the values $e^a=-0.028(-1/2,-1/2,1)$ and $u_s^a=0.038(1,-1,0)$ are derived from the data of Ref 2. That $u_s^z=0$ implies $\theta_2=-\theta_1+\pi$; substituting this into Eqs. (10) leads to equations for θ_1 and λ/K_1 which may be solved if K_2/K_1 is given. Results are listed in Table I.

We now turn to the value of A. The assumption of a two-sublattice distortion and the condition $h_i=0$ implies that Eq. (7) becomes

$$E=\frac{1}{2}A[\cos(6\theta_1)+\cos(6\theta_2)]+3\kappa\cos(2\theta_1-2\theta_2). \tag{11}$$

By minimizing Eq. (11) and using $\theta_2=\theta_1+\pi$ we find

$$\frac{A}{\kappa}=-\frac{-2\sin(4\theta_1)}{\sin6\theta_1}. \tag{12}$$

Values for A/κ are also listed in Table I.

The most important information contained in Table I is that the basic Jahn-Teller energy E_0 is much greater than the stiffness κ which orients the distortions from site to site. Indeed, from Eq. (6) the ratio may be seen to be $\frac{1}{3}K_2/(K_1+K_2)$; as it is unlikely that the Mn-Mn force constant $K_2>$ the Mn-O force constant K_1, the ratio is less than 1/6. The structural transition occurring at $T_s\approx800$ K in LaMnO$_3$ is therefore of the order-disorder type, and we may expect local distortions to persist for $T>T_s$.

From Table I it is also clear that the anisotropy energy is not small, although the precise value depends sensitively on K_2/K_1.

Now consider magnitudes of energy scales. The basic scale is K_1; this is related to the frequency of an oxygen bond stretching phonon $\omega_{\rm ox}$ by

$$\omega_{\rm ox}=\sqrt{\frac{2K_1/b^2\hbar^2}{M_{\rm ox}}}. \tag{13}$$

The factor of 2 arises because there are two Mn-O bonds in Eq. (2). Estimating 100 meV$\gtrsim\hbar\omega_{\rm ox}\gtrsim30$ meV and using $b=4$ Å gives

$$300\ \text{eV}\gtrsim K_1\gtrsim30\ \text{eV}. \tag{14}$$

I am unaware of measurements of the phonon spectrum in LaMnO$_3$. If, however, it is assumed that the phonon spectrum has a rather weak doping dependence one may use optical data from La$_{1.85}$Sr$_{0.15}$MnO$_3$.[12] The highest-lying phonon modes were observed at $\omega_{\rm ph}\sim70$ meV. It is reasonable to assume that these are the bond-stretching oxygen modes of interest and that these modes are only weakly dispersive; thus, one may identify $\omega_{\rm ph}$ with $\omega_{\rm oxy}$ and estimate $K_1\approx200$ eV.

An alternative estimate may be obtained from the mean-field approximation to the structural transition temperature $T_s\approx750$ K. This is shown in Appendix E to be $T_s^{\rm MF}\approx3\kappa$, and mean-field theory overestimates T_s; so

$$\kappa>20\ \text{meV}. \tag{15}$$

This bound on κ yields K_2/K_1-dependent bounds for K_1 ranging from $K_1>220$ eV ($K_2/K=0.1$) to $K_1>50$ eV ($K_2/K_1=1$). Values of $K_2/K_1\gtrsim0.5$ are most consistent with estimates of $\omega_{\rm oxy}\lesssim50$ meV, those of $K_2/K_1<0.5$ with $\omega_{\rm oxy}\gtrsim50$ meV. Combining this with the estimate $K_1\approx200$ eV suggests $A\sim\kappa$. This estimate is consistent with estimates given in a standard review[13] that typical anharmonicity energies are of order a few hundred kelvin.

The estimates of K_1 imply Jahn-Teller energies E_0 ranging from ≈100 meV at the low end ($K_1\sim30$ eV) to 1 eV at the high end ($K_1\sim300$ eV). The estimate $\omega_{\rm oxy}=70$ meV implies $E_0\approx0.6$ eV, slightly larger than the largest Jahn-Teller energy listed in a standard review.[13] In any event, because the energy splitting between the two d levels is $4E_0$, it is safe to assume that at any reasonable temperature the splitting is frozen in. Unfortunately the splitting is difficult to measure directly because most methods for coupling to the d level involve changing the valence of the Mn, which would bring other physics in to play. The transition should be Raman active, though.

To summarize, it has been shown in this section that the Jahn-Teller energy of LaMnO$_3$ may be written

$$E_{x=0}=\kappa\sum_{ia}\cos(2\theta_i+2\psi_a)\cos(2\theta_{i+a}+2\psi_a)$$

$$+A\sum_i\cos6\theta_i. \tag{16}$$

If $A\gtrsim T_s$, then it is reasonable to assume that at each site θ_i is near one of the three angles favored by the anharmonicity term, so that the system may be mapped on to a three-state Potts model as previously noted.[8] Details are given in Appendix D. The result is conveniently written in a notation in which the state of site i is represented by a vector $\mathbf{Q}_i$ with a 1 in one place and 0 in the other two places; $\mathbf{Q}_i=(1,0,0)$

implies there is a Jahn-Teller distortion with the long axis along x, $\mathbf{Q}_i=(0,1,0)$ means y and $(0,0,1)$ means z. Then

$$E_{\mathrm{Potts}}=\kappa\sum_{ia}\vec{Q}_i\mathbf{I}^a\vec{Q}_{i+c}+J'\sum_{ia}\vec{Q}_i\cdot\vec{Q}_{i+2a}, \tag{17}$$

with $\mathbf{I}^a$ a bond-direction-dependent interaction given in Eq. (D3) and $J'<0$ a ferromagnetic interaction between "straight-line" second neighbors, which is of order κ/A and was apparently not neglected in previous work. The second-neighbor interaction is an approximation to the true interaction, as discussed in Appendix D. The three state Potts model has a transition in the x-y universality class as, therefore, does Eq. (16). The second-neighbor "ferromagnetic" coupling lifts the degeneracies which lead to subtleties in the behavior of the usual Potts model. The estimates of A suggest that the extreme Potts limit will not provide a good quantitative description of LaMnO_3.

IV. HOLES

This section discusses the effects of added holes. It is clear from Eq. (7) that a hole on site i eliminates the Jahn-Teller distortion on site i and leads to a potential, $\beta\kappa\cos(2\theta_{i+b}+2\psi_b)$, which acts to orient the distortion on site $i+b$ so that its long axis is along $\hat{b}$. Thus added holes lead both to site dilution and to a field which tends to orient some of the neighbors of the hole in directions not compatible with long-range order.

If $A>0$ (as seems to occur in LaMnO_3), the angles favored by holes are compatible with the angles favored by anharmonicity; if $A<0$ an interesting competition arises, which will not be discussed here.

In the $A\gg 0$ limit the effect of added holes is particularly transparent. By following the derivation that led to Eq. (17) one finds that a hole on site i produces a term in the energy

$$E^i_{\mathrm{hole}}=\beta\kappa\sum_b\vec{R}^b\cdot\vec{Q}_{i+b}, \tag{18}$$

with $R^x=(-1,1/2,1/2)$, etc. Thus in this limit a hole manifestly produces a field which tends to orient the spins on neighboring sites.

A Monte Carlo investigation based on Eq. (7) or on Eqs. (17), (18) would be desirable. Here simple arguments are given to estimate $T_s(x)$. Assume the hole positions are uncorrelated with each other or with the configuration of Jahn-Teller orderings. To estimate the critical concentration x_c, of holes at which ordering vanishes, note that for site-diluted systems ($\beta=0$), T_s vanishes when the occupied sites do not percolate.[14] For the simple cubic lattice, the percolation threshold is about $p_c=0.3$,[14] and so $x_c(\beta=0)=0.7$. Of course for such large values of x the model is not valid. For $\beta\to\infty$, each hole eliminates five sites (itself and four neighbors, two remain approximately correctly oriented), implying $1-5x_c=0.3$ or $x_c(\beta\to\infty)\cong 0.14$.

Alternatively, one may use mean-field theory to estimate $T_s(x)$. The fundamental object in mean-field theory is the probability distribution $P(\theta)$ of the angle on a distinguished site in an effective field depending on the average values of the angles on the adjacent sites and on whether or not holes are present. The assumption of uncorrelated holes implies

$$P(\theta)=\sum_{\{h_a\}}\frac{e^{-E(\theta,\{h_a\})/T}}{Z(\{h_a\})}x^{n_h}(1-x)^{6-n_h}. \tag{19}$$

Here $\{h_a\}$ is a distribution of holes on sites adjacent to the distinguished one, n_h is the number of holes in that particular configuration, and

$$Z(\{h_a\})=\int_0^\pi\frac{d\theta}{\pi}e^{-E(\theta,\{h_a\})/T}. \tag{20}$$

The energy may be written in terms of the average values of the cosine and sine on the other sublattice, $c=\langle\cos 2\theta\rangle$ and $s=\langle\sin 2\theta\rangle$, as

$$E(\theta,\{h_a\})=2\kappa\sum_a(1-h_a)\cos(2\theta+2\psi_c)$$
$$\times[(c\cos 2\psi_a-s\sin 2\psi_c)1-h_a+\beta h_c]. \tag{21}$$

The quantities c and s satisfy a self-consistency equation; the linearized equation giving T_s may be written

$$c=-\int_0^\pi\frac{d\theta}{\pi}P(\theta)\cos 2\theta. \tag{22}$$

The derivation and evaluation of this equation are given in Appendix E. An analytic treatment is not simple except in the limits $A\to 0$ or $A\to\infty$ (arbitrary β) and $\beta\to 0$ or $\beta\to\infty$ (arbitrary A). For $A=0$,

$$1=\frac{3\kappa}{T_s}\left[1-x\left(1+\frac{4I_1^2}{I_0^2}+\frac{I_2}{I_0}\right)\right]. \tag{23}$$

Here the I_n are Bessel functions of imaginary argument $i\beta/T_s$.

In the $A\to\infty$ limit, $T_x(\beta,x)$ satisfies

$$1=\frac{3\kappa}{T_s}\left[1-x\frac{6-3e^{-3\beta/2T_s}+6e^{-3\beta/T_s}}{(1+2e^{-3\beta/2T_s})^2}+Ox^2\right]. \tag{24}$$

For $\beta=0$, the x^2 and higher terms vanish and $T_s=3\kappa(1-x)$ as expected for simple site dilution.[14] The mean-field theory overestimates the x_c at which T_s vanishes because it does not contain the physics of percolation. As β/T_s is increased, the coefficient of dT_s/dx increases; for $\beta/T_s\to\infty$, $T_s\to 3\kappa(1-6x)$, suggesting $x_c\approx 0.16$. Comparison to the percolation argument given previously suggests that this is an underestimate. The general result, however, of a $T_s(x)$ which drops rapidly as x is increased and depends somewhat on model parameters (and so on materials) is in reasonable accord with data. Note, however, that at low T quantum effects involving motion of holes will become important.

V. CONCLUSION

A classical model for $\mathrm{La}_{1-x}A_x\mathrm{MnO}_3$ has been analyzed. It is known that doping on the La site changes the valence of the Mn site in such a way that the mean number of outer d-shell electrons on the Mn is $1-x$. The holes were assumed to be classical, so that each Mn site is occupied, with probability $1-x$, or empty, with probability x. The hypothesis of classical holes has been shown to be consistent with the resistivity at all x and $T>400$ K and for $x<x_{\mathrm{cond}}\sim 0.3$ and all T.[5]

Because the outer Mn d-orbital is twofold degenerate, a Jahn-Teller distortion of the surrounding oxygen octahedron which lowers the local cubic symmetry to tetragonal may occur about each occupied Mn site, while a breathing mode distortion may occur around each unoccupied site. Each oxygen is shared by two Mn ions, and so distortions on adjacent sites are coupled. The coupling was determined from a classical harmonic approximation to the lattice dynamics. The parameters of the model were determined by fitting to the structural data obtained for $\mathrm{LaMnO_3}$. The principal results are the following.

(1) The basic energy gained in a local Jahn-Teller distortion, $E_0 \gtrsim 0.1$ eV. The estimate $E_0 \approx 0.6$ eV was obtained using a phonon frequency estimated from an optical measurement on $\mathrm{La_{1.85}Sr_{.15}MnO_3}$. A direct measurement of the splitting $4E_0$ between the two d levels would be desirable. The distortions are in any event well formed at any relevant temperature and the structural transition is to be regarded as an order-disorder transition, at which local Jahn-Teller distortions become spatially decorrelated, but do not disappear.

(2) The model describing the transition is given in Eq. (7) and may be approximated either by an antiferromagnetic x-y model with a modest threefold anisotropy or by a three-state Potts model with an antiferromagnetic first-neighbor interaction and a weak second-neighbor interaction. Which model is more nearly correct depends on whether the anharmonicity parameter A is larger or smaller than the stiffness κ which orients the distortions. By combining an optical measurement of the highest phonon frequency in $\mathrm{La_{1.85}Sr_{0.15}MnO_3}$ with a calculation of T_s the estimate $A\sim\kappa$ was obtained.

(3) Added holes disrupt the long-range order by producing an effectively random field, which misorients nearby Jahn-Teller distortions. It would be very interesting if it were possible to observe directly this local misorientation. This random field effect was shown by various mean-field calculations to lead to a rapidly decreasing $T_s(x)$, in qualitative accord with data. A Monte Carlo investigation of the problem would be useful.

The results in this paper substantiate to some degree the proposal[4,5] that electron-lattice interaction is so strong that the high-T cubic (or pseudocubic) $0.2\lesssim x\lesssim 0.4$ phase of $\mathrm{La_{1-x}A_xMnO_3}$ should be modeled as a disordered array of polarons. The results presented here provide a basis for calculating polaron binding energies and mobilities, both for $0.2\lesssim x\lesssim 0.4$ and high T and for low x at all T.

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APPENDIX A: DERIVATION OF ENERGY

This appendix outlines the derivation of Eq. (7) from Eqs. (2), (3), and (5) and discusses anharmonic terms. Define

$$u_i^a = \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{R}_i} u_{\mathbf{k}}^a \tag{A1}$$

and similarly $\delta_{\mathbf{k}}^a$. Now $\delta_{\mathbf{k}}^a$ may be decoupled from E_{latt}, Eq. (2), by defining

$$\bar{\delta}_{\mathbf{k}}^a = \delta_{\mathbf{k}}^a - \frac{1}{2}\,\frac{K_1(1+e^{i\mathbf{k}_a})}{2K_1+K_2-K_2\cos\mathbf{k}_a}\,u_k^a . \tag{A2}$$

$\bar{\delta}_{\mathbf{k}}^a=0$ gives the equilibrium positions about which the Mn ions fluctuate. After decoupling, the relevant part of the lattice energy may be written

$$E_{\mathrm{latt}} = K_1 \sum_{ka} F(k_a)\, u_{\mathbf{k}}^a u_{-\mathbf{k}}^a , \tag{A3}$$

with

$$F(k_a) = \frac{1}{2}\,\frac{(K_1+2K_2)(1-\cos k_a)}{K_1+K_2-K_2\cos k_a} . \tag{A4}$$

The interaction energies are most conveniently written in terms of the variables $c_{\mathbf{k}}^a$ defined via

$$c_{\mathbf{k}}^a = \sum_i e^{i\mathbf{k}\cdot\mathbf{R}_i}(1-h_i)\cos 2(\theta_i+\psi^a), \tag{A5}$$

where $\psi^z=0$, $\psi^x=-\pi/3$, and $\psi^y=\pi/3$ were introduced in Eq. (7). Combining Eqs. (3), (4), (A5), gives

$$E_{\mathrm{JT}} = \lambda \sum_{ka} (1-e^{-ik_a})\, u_{\mathbf{k}}^a u_{-\mathbf{k}}^a ,$$

$$E_{\mathrm{hole}} = \beta\lambda \sum_{ka} h_{\mathbf{k}} (1-e^{-ik_a})\, u_{-\mathbf{k}}^a . \tag{A6}$$

The displacement u may be eliminated by writing E in terms of

$$\bar{u}_{\mathbf{k}}^a = u_{\mathbf{k}}^a - \frac{\lambda(1-e^{-ik_a})}{2K_1F(k_a)}(c_{\mathbf{k}}^a+\beta h_{\mathbf{k}}). \tag{A7}$$

Again $\bar{u}=0$ defines the average state about which the oxygen atoms fluctuate. The electronic part of the energy may then be written

$$E = -\frac{1}{2}\,\frac{\lambda^2}{K_1}\sum_{ka}\frac{1-\cos k_a}{F(k_a)}(c_{\mathbf{k}}^a+\beta h_{\mathbf{k}})(c_{-\mathbf{k}}^a+\beta h_{-\mathbf{k}}). \tag{A8}$$

Fourier transformation yields Eq. (7) except for the term proportional to A. This term arises from a lattice anharmonicity of the form $\Sigma_i v_i^3$. Use of Eq. (A7) yields several terms, of which the largest is $A\cos(6\theta)$.

APPENDIX B: ANALYSIS OF STRUCTURE

In this appendix the $\mathrm{LaMnO_3}$ structural data obtained by Ellemans *et al.*.[2] are analyzed. The magnitudes of the atomic displacements observed in $\mathrm{LaMnO_3}$ in Ref. 2 are somewhat greater than those reported in previous work.[15] Indeed, the displacements reported for $\mathrm{LaMnO_3}$ by Ref. 15 are very similar to those reported by Ellemans *et al.*, for $\mathrm{La_{1.95}Ca_{0.05}MnO_3}$.[2] It will be assumed here that the larger values are most representative of the undoped material, and that the $LaMnO_3$ sample studied in Ref. 15 was inadvertently doped.

The actual crystal structure of $LaMnO_3$ is complicated; for example, every Mn-O-Mn bond is buckled. It is assumed here that the important quantities are the Mn-O bond lengths, and that the remaining distortions are subsidiary, being driven by rotations of the (distorted) MnO_6 octahedra required to fit the rigid MNO_6 octahedra into a lattice with lattice constants smaller than twice the Mn-O distances.

$LaMnO_3$ was found to be orthorhombic, with three unequal Mn-O distances, which are

$$\begin{aligned} u_x &= 2.187 \text{ Å}, \\ u_y &= 1.905 \text{ Å}, \\ u_z &= 1.956 \text{ Å}. \end{aligned} \tag{B1}$$

Here u_x, u_y are the distances most nearly parallel to the nearest-neighbor Mn-Mn bonds in the basic (orthorhombic a-c) plane. The x-y directions are about 45° rotated from the orthorhombic a-c axes. u_z is the distance most nearly parallel to the orthorhombic b axis.

The z oxygen ion is equidistant from the Mn above and below it; the x and y oxygen ions are not equidistant from the in-plane Mn; indeed, if one moves from one Mn to its in-plane nearest neighbor, the roles are reversed. We therefore assume that the observed Mn-O bond lengths have been obtained from an ideal peroviskite structure with Mn-O distance of $u^0 = (u_x u_y u_z)^{1/3} \cong 2.01$ Å by composing a uniform tetragonal distortion $\Delta^u = -0.112$ Å $(1,-1/2-1/2)$ and a staggered distortion $\Delta^s = 0.15$ Å $(1,-1,0)$. The mean lattice constant is 4 Å; thus Δ^u corresponds to a uniform strain components $e^{xx} = e^{yy} = 0.014$, $e^{zz} = -0.028$, while the staggered distortion is $u^s = 0.038(1,-1,0)$.

APPENDIX C: SOLUTION OF THE MEAN-FIELD EQUATIONS

In this appendix details are given of the solution of the mean-field equations and of the energetics of small deviations from the mean-field solution.

Solution: Assume a two sublattice solution with $\theta = \theta_1$ on one sublattice and $\theta = \theta_2$ on the other. Take $A > 0$ without loss of generality and choose units in which $3\kappa = 1$. Write

$$\theta_{1,2} = \frac{2n_{1,2}+1}{6}\pi + \delta_{1,2}, \tag{C1}$$

with

$$-\pi/6 \leqslant \delta_{1,2} \leqslant \pi/6. \tag{C2}$$

From Eq. (7) one has

$$E_{\mathrm{MF}} = \cos\left[\frac{2(n_1-n_2)\pi}{3} + 2\delta_1 - 2\delta_2\right] - \frac{a}{6}(\cos 6\delta_1 + \cos 6\delta_2), \tag{C3}$$

with $a = A/\kappa > 0$.

Minimizing yields

$$2\sin\left[\frac{2(n_1-n_2)\pi}{3} + 2\delta_1 - 2\delta_2\right] = a\sin 6\delta_1 \tag{C4}$$

and

$$\sin 6\delta_1 = -\sin 6\delta_2. \tag{C5}$$

Equation (C5) implies either $\delta_1 = -\delta_2$ or $\delta_1 = \delta_2 + (2n+1)\pi/6$; the latter solution would imply that the anharmonicity energy vanishes. Such an extremum cannot produce an absolute energy minimum. If $\delta_2 = -\delta_1$, then Eq. (C4) may be solved. Define

$$\delta = \frac{\pi}{12} - \frac{1}{2}\arcsin\left[\sqrt{\frac{1+a^2}{4a^2}} - \frac{1}{2a}\right]. \tag{C6}$$

Then $\delta_1 = -\delta_2 = \delta$ if $n_1 - n_2 = 1$ or -2 and $\delta_1 = -\delta_2 = -\delta$ in $n_1 - n_2 = -1$ or 2. A different formula applies if $n_1 = n_2$; however, this case may be seen not to lead to the global energy minimum because if $n_1 = n_2$, then the intersite term is positive unless $\pi/8 \leqslant |\delta| \leqslant \pi/6$, in which case the anharmonicity term is positive. The mean-field energy is thus minimized by any of the six configurations with $n_1 \neq n_2$ and appropriate δ_1 and δ_2.

It is instructive to suppose that at all but one of the sites the angles take values minimizing E_{MF} and to study the energy function E_0 of the remaining angle. Assume the isolated site is on the "1" sublattice and $n_1 = 0$. Then

$$E_0 = 2\cos\left[2\theta - \frac{\pi}{3}2\delta\right] + \frac{a}{3}\cos 6\theta. \tag{C7}$$

For $a < a^* = 4/3$, Eq. (C7) has only one minimum, at the θ which satisfies the mean-field equation. For $a > a^*$ there are three minima. For $a \gg a^*$ these occur at

$$\theta_n = \frac{(2n+1)\pi}{6} + \frac{2\sin 2n\pi/3}{3a} + O\frac{1}{a^2} \tag{C8}$$

and correspond to energies

$$E_n = -\frac{a}{3} + 2\cos\frac{2n\pi}{3}\,\frac{2}{\sqrt{3}a}\sin\frac{2n\pi}{3}. \tag{C9}$$

This is the expected form of the energy of a three-state Potts model with a first-neighbor "antiferromagnetic" and second-neighbor "ferromagnetic" interactions. A precise mapping is discussed in Appendix D.

Small deviations: Assume that on every site the angle is close to one of the two-sublattice solutions; thus, if $a = 1,2$

$$\theta_i = \theta_a + \psi_i, \tag{C10}$$

with θ_a given by Eqs. (C1), (C6) according to whether i is on sublattice 1 or 2 and ψ small. Substituting Eq. (C10) into Eq. (7) and expanding yields

$$E = E_{\mathrm{MF}} + \sum_{\mathbf{k}} \omega_{\mathbf{k}}^2 \psi_{\mathbf{k}} \psi_{-\mathbf{k}}. \tag{C11}$$

The energy $\omega_{\mathbf{k}}^{(n_1,n_1)}$ depends on the quantities n_1, n_2 describing the possible ordered states. There are three independent choices $[(n_1,n_2)=(0,1),\ (1,2),\ (0,2)]$, each picks out a preferred axis $a=x,y,z$. We have $[\gamma_{\mathbf{k}}=1-(\cos k_x+\cos k_y+\cos k_z)]$

$$\omega_{\mathbf{k}}^{(0,1)}=\omega_{\mathbf{k}}^{x}=6a\cos 6\delta+4\cos\left(\frac{\pi}{3}-4\delta\right)\gamma_{\mathbf{k}}-4\left[\cos k_x-\frac{1}{2}(\cos k_y+\cos k_z)\right]. \tag{C12}$$

Similarly $\omega^{1,2}=\omega^{y}$ and $\omega^{0,2}=\omega^{z}$. Note that because of the relation of the angles ψ to the physical lattice distortions, a nearly uniform variation of ψ corresponds to a nearly staggered variation of the physical lattice distortions. For physically relevant values of a the gap is relatively large and the dispersion small.

APPENDIX D: DERIVATION OF THE POTTS MODEL

This appendix gives the details of the derivation of Eq. (17) from (Eq. 7). It is assumed A is so large that only angles near those minimizing the anharmonicity energy $A\cos 6\theta_i$ are allowed. Thus write

$$\theta_i=\phi_i^{\alpha}+\delta_i, \tag{D1}$$

with ϕ_i^{α} one of $\phi^{x}=5\pi/6$, $\phi^{y}=\pi/6$, and $\phi^{z}=\pi/2$, and δ_i a small deviation. Note that the Jahn-Teller distortion corresponding to ϕ^{a} is $u_a-\frac{1}{2}(u_b+u_c)$. Substituting Eq. (D1) into Eq. (7) and expanding gives

$$\frac{E}{3\kappa}=-\frac{Na}{3}+\frac{1}{3}\sum_{ia}\cos[2\phi_i^{\alpha}+2\psi_a]\cos[2\phi_{i+a}^{\alpha}+2\psi_a]+6a\sum_{i}\bar{\delta}_i^2-\frac{8}{27}a\sum_{iab}\sin[2\phi_i^{\alpha}+2\psi_a]\sin[2\phi_i^{\alpha}+2\psi_b]\cos[2\phi_{i+a}^{\beta}+2\psi_c]\cos[2\phi_{i+b}^{\gamma}+2\psi_b]. \tag{D2}$$

Here N is the number of sites in the crystal, $a=A/\kappa$, and $\bar{\delta}_i=\delta_i-\delta_i^{\min}$, with $\partial E/\partial\delta_i^{\min}=0$. In the large-$A$ limit the coefficient of the $\bar{\delta}$ term is large, and so fluctuations in $\bar{\delta}$ may be neglected.

The energy may be more conveniently written in a discrete notation. Denote the state on site i by the continuous variable δ_i and define a discrete quantity $\mathbf{Q}_i$ which indicates to which of ϕ_x,ϕ_y,ϕ_z the angle θ_i is nearest. Choose $\mathbf{Q}_i$ to be a three-component vector with a 1 in one place and 0 in the other two. $\mathbf{Q}_i=(1,0,0)$ means θ_i is close to ϕ_x, $\mathbf{Q}_i=(0,1,0)$ means θ_i is close to ϕ_y and $\mathbf{Q}_i=(0,0,1)$ means θ_i is close to ϕ_z. The interaction term of order is then a 3×3 matrix $\mathbf{I}^{a}$, which depends on the direction $\hat{a}$ of the bond connecting the two sites. One finds

$$\mathbf{I}^{x}=\frac{1}{3}\begin{pmatrix}1 & -1/2 & -1/2\\ -1/2 & 1/4 & 1/4\\ -1/2 & 1/4 & 1/4\end{pmatrix}. \tag{D3}$$

$\mathbf{I}^{y},\mathbf{I}^{z}$ are obtained by permuting both row and column in the obvious way.

The term of order $1/a$ is a rather complicated three-site interaction; however, the important physics of this term is the coupling it induces between sites on the same sublattice. To determine this coupling it is convenient to restrict attention to configurations (favored by the order 1 term) in which adjacent sites are in different Potts states, i.e., to terms in the order $1/a$ term in Eq. (D2) in which $\beta\neq\gamma$. If site i is taken to be in state $\alpha=x$, then the only nonconstant terms are when $a=-b\neq\hat{x}$. If $a=\pm\hat{y}$, then the energy is $-4/9a$ if both sites are in the "y" state, $-1/9a$ if both are in the "z" state, and $1/9a$ if the two are in different states; i.e., we may write

$$E^{(2)}=-\frac{1}{9a}\sum_{ib'}\vec{Q}_i^{\alpha}(\vec{Q}_{i+b}J_b^{\alpha}\vec{Q}_{i+b'}, \tag{D4}$$

with $b=\pm x,y,z$ and

$$J_b^{x}=\begin{pmatrix}0 & 0 & 0\\ 0 & 4 & -2\\ 0 & -2 & 1\end{pmatrix}, \tag{D5}$$

etc.

The principal effect of $E^{(2)}$ is to lift the degeneracies of the antiferromagnetic three-state Potts model; this effect may be mimicked by a simple second-neighbor ferromagnetic interaction with magnitude J' fixed, e.g., by the requirement that it reproduce Eq. (C9).

APPENDIX E: MEAN-FIELD T_s WITH HOLES

In the presence of a concentration x of holes, one expects $T_s(x)=T_{c0}(1-\alpha x)$. In this Appendix α is derived using a mean-field theory. In leading order in x one need only consider configurations in which one of the six neighbors of the distinguished site, say, the one in the b direction, has a hole. From Eq. (21) one has

$$E_b(\theta)=2\kappa\cos(2\theta+2\psi_b)[c\cos 2\psi_b-s\sin 2\psi_b+\beta]+4\sum_{p=\pm 1}\cos\left(2\theta+2\psi_b+\frac{2\pi p}{3}\right)\left[c\cos\left(2\psi_b+\frac{2\pi p}{3}\right)-s\sin\left(2\psi_b+\frac{2\pi p}{3}\right)\right]. \tag{E1}$$

Substituting Eq. (E1) into Eqs. (19), (20), expanding in c and s, rearranging, and discarding terms proportional to $\cos 2\theta\sin 2\psi_b$ or $\sin 2\theta\cos 2\psi_b$, which will not contribute to averages of interest, gives

$$Z_b = \int_0^{\pi} \frac{d\theta}{\pi} e^{-A\cos 6\theta/T - \beta\cos 2\theta/T} \left[1 - \frac{4c\kappa}{T} \cos 2\theta \cos 2\psi_b - \frac{6c\kappa}{T} \sin 2\theta \sin 2\psi_b \right] \tag{E2}$$

and, using also Eq. (22) and the results of Appendix C,

$$1 = \frac{3\kappa}{T_s}[1-6x] - \frac{1}{c}\sum_b \frac{1}{Z_b}\int_0^{\pi} \frac{d\theta}{2\pi} e^{A\cos 6\theta/T - \beta\cos 2\theta/T} \left[1 - \frac{4c\kappa}{T_s}\cos 2\theta \cos 2\psi_b - \frac{6c\kappa}{T_s}\sin\theta \sin 2\psi_b \right] \times \cos(2\theta - 2\psi_b). \tag{E3}$$

The integrals in Eqs. (E2), (E3) may be expressed in terms of products of Bessel functions $I_n(A/T)I_m(\beta/T)$. The expressions become simple when $A \to 0$ or ∞ or $\beta \to 0$ or ∞, and lead after straightforward calculations to Eqs. (22), (23).

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