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Paramagnetic phase in single-crystal $LaMnO_3$

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We report the observation of a peculiar conductive phase with ferromagnetic interactions and a Curie-Weiss paramagnetism above the cooperative Jahn-Teller orbital-ordering temperature T_{JT} in a single crystal of the single-valent compound $LaMnO_3$. A positive Weiss constant increases discontinuously on raising the temperature through T_{JT}, but the Curie constant remains unchanged. Above T_{JT}, a nearly temperature-independent resistivity $\rho(T)$ and thermoelectric power $\alpha(T)$ that, unlike below T_{JT}, are insensitive to the oxidation state of the MnO_3 array are suggestive of charge transport by vibronic charge carriers. [S0163-1829(99)51746-3]

The geometric tolerance factor $t \equiv (A\text{-O})/\sqrt{2}(M\text{-O})$ is a measure of the mismatch between the equilibrium (A-O) and (M-O) bond lengths of an AMO_3 perovskite. Accommodation to a $t<1$ is accomplished by a cooperative rotation of the corner-shared $MO_{6/2}$ octahedra, which bends the M-O-M bond angles to $(180°-\phi)$. Rotations about the cubic [111] axis give rhombohedral symmetry with bending angle ϕ_R, and rotations about the cubic [110] axis give orthorhombic symmetry with mean bending angle $\phi_O > \phi_R$ In the $L_{1-x}A_xMnO_3$ (L=lanthanide, A=alkaline-earth) perovskites, every octahedral-site Mn atom has a localized t^3 configuration of spin $S=3/2$, and strong intra-atomic exchange removes the spin degeneracy of the twofold-degenerate e orbitals. In $LaMnO_3$, a cooperative Jahn-Teller ordering of the occupied e orbitals at the Mn(III):t^3e^1 ions removes the e-orbital degeneracy and lowers the c/a ratio of the orthorhombic structure; we distinguish the orbitally disordered and orbitally ordered phases by the notation O and O' orthorhombic. The orbital ordering signals that the e electrons are localized. At $x=0.5$, charge ordering localizes the e electrons; the Mn(IV):t^3e^0 and Mn(III):t^3e^1 sites are distinguishable, and orbital ordering at the Mn(III) ions results in tetragonal symmetry with a complex type CE antiferromagnetic order.[1,2,3] Whereas the antiferromagnetic, orbitally ordered O' and CE phases are insulators, the orbitally disordered phases are ferromagnetic and conductive. The Curie temperature T_c of the ferromagnetic phase increases sharply with x and/or t in the O phase near the O'/O phase boundary, and a first-order metallic-polaronic transition at T_c becomes second order as T_c increases to a maximum value near $x=0.38$. In the range $0.38<x<0.5$, T_c decreases with increasing x and, with smaller t, electron-electron Coulomb interactions induce a charge ordering at $x=0.5$ that localizes the e electrons.

Magnetic Mn-O-Mn interactions in the manganese-oxide perovskites involve charge transfers, real or virtual. Real charge transfers are treated in first-order perturbation theory and give rise to ferromagnetic double-exchange interactions. Virtual charge transfers are treated in higher-order perturbation and give rise to superexchange interactions that may be either antiferromagnetic or ferromagnetic. Superexchange interactions occur in insulators, and double-exchange interactions are found in metallic oxides and were first postulated to account for isotropic ferromagnetism in the mixed-valent perovskites $La_{1-x}A_xMnO_3$ (A=alkaline earth). A cooperative Jahn-Teller ordering of the twofold-degenerate e orbitals at the Mn(III):t^3e^1 ions in $LaMnO_3$ gives anisotropic superexchange interactions, ferromagnetic (001) plans coupled antiferromagnetically along the c axis;[1,2,4,5] and orbital disorder in the $LaMn_{1-x}Ga_xO_3$ system, which also contains only Mn(III) ions, gives isotropic ferromagnetic superexchange coupling.[6] The original double-exchange interaction postulated by Zener[7] involves formation of two-manganese Mn(III)-O-Mn(IV) polarons that move diffusively with no motional enthalpy. The de Gennes[8] double-exchange model couples localized t^3-configuration spins by intra-atomic exchange with itinerant electrons in a partially filled σ^* band of e-orbital parentage. It differs from indirect exchange by its treatment of the mobile e electrons, which are assumed to tunnel from a Mn(III) to a Mn(IV) only after the mobile spin has become aligned with the localized spin on the donor atom. Extrapolation of the de Gennes double-exchange model to $LaMnO_3$ is not possible; coupling of localized t^3-configuration spins by itinerant e electrons in a partially filled σ^* band in single-valent $LaMnO_3$ would be better treated by the Yafet-Kittel-Kasuya-Yosida (YKKY) indirect-exchange model. However, if the conducting spins are vibronic in $LaMnO_3$, a double-exchange interaction may be applicable.

Jonker[9] has reported a positive Weiss constant $\theta<T_N$ of the Curie-Weiss paramagnetism of the antiferromagnetic O' phase below T_{JT} and a sharp increase in the Weiss constant to a $\theta>T_N$ in the O phase above T_{JT}. A question arises whether the apparent isotropic ferromagnetic interactions of the orbitally disordered O phase of single-valent $LaMnO_3$ should be described by a superexchange interaction in association with locally cooperative, dynamic Jahn-Teller deformations or by a double-exchange interaction. In order to clarify this question, we have undertaken a careful investigation on single-crystal $LaMnO_3$ of the transport and magnetic susceptibility data from room temperature to above T_{JT}. The early work of Jonker[9] was done on a polycrystalline sample at a time when control of the oxygen stoichiometry was less precise.

Floating-zone (FZ) crystal growth in an infrared- (IR) heated furnace gives pure, large single crystals. Rodriguez-

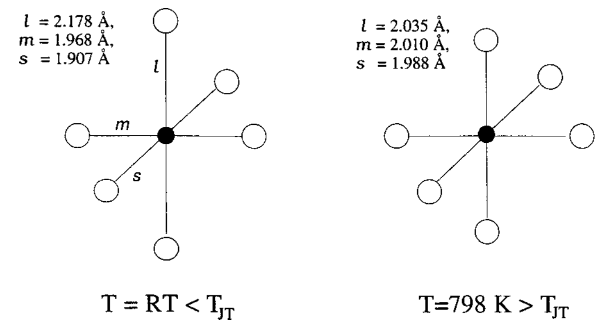

FIG. 1. The change in Mn-O bond lengths on crossing T_{JT} after Ref. 10.

Carvajal *et al.*[10] have used this technique to show that $T_{JT} = 750$ K in stoichiometric $LaMnO_3$ and decreases sensitively with Mn(IV) concentration.They also showed that the mean ⟨Mn-O⟩ bond length changes little on crossing T_{JT} although the orthorhombic distortion measured by diffraction changes significantly (Fig. 1). A small change in ⟨Mn-O⟩ means little change in the mean potential energy of the electrons and therefore little discontinuity in the Jahn-Teller stabilization on passing from orbital order to disorder. We may infer an orbital order-disorder transition at T_{JT} with a dynamic Jahn-Teller stabilization of the *e* electrons persisting into the high-temperature *O*-orthorhombic phase.

We obtained single-crystal $LaMnO_3$ by FZ growth in a flow of high-purity Ar gas with an IR-heated image furnace (NEC SC-35 MD). The starting ceramic rods of $LaMnO_3$ were the product of a reaction between La_2O_3 (99.995%) and Mn_2O_3 (99.995%) in a 1:1 ratio. The high-temperature transport and magnetic measurements were carried out in a vacuum of 10^{-3} torr with, respectively, homemade apparatus and a commercial superconducting quantum interference device (SQUID) magnetometer (Quantum Design). Both powder diffraction and Laue back diffraction were used to verify the structure and single-crystal character of the sample. The results of our transport measurements, shown in Fig. 2, have two interesting features.

(i) *An irreversible change from* α(300 K)$=-600$ μV/K *to about* $+550$ μV/K *on thermal cycling to* 1100 K. Small-polaron conduction by a single charge carrier would give a

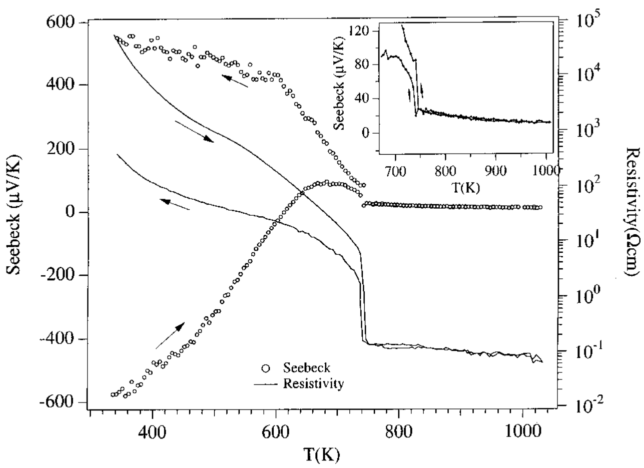

FIG. 2. Resistivity $\rho(T)$ and thermoelectric power $\alpha(T)$ taken on cycling a virgin single crystal from room temperature to 1100 K.

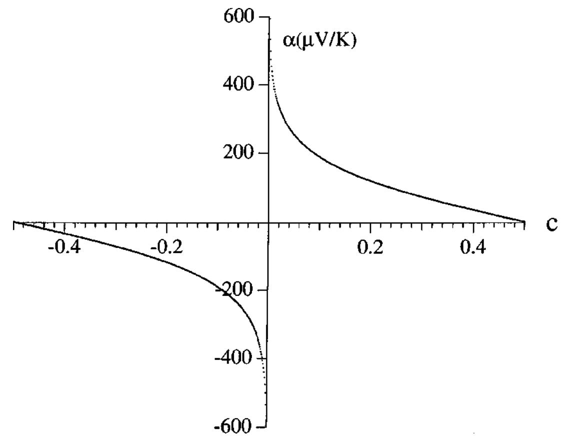

FIG. 3. Theoretical $\alpha(T)$ vs c curves based on Eq. (1).

temperature-independent thermoelectric power dominated by the statistical term:

$$\alpha = -(k/e)\ln[(1-c)/c], \tag{1}$$

where c is the fraction of Mn sites occupied by a charge carrier and the spin degree of freedom is lifted by the strong intra-atomic exchange. Near stoichiometry, two types of charge carriers may be present, but with only one dominating at room temperature to give a large negative or large positive value of α(300 K) for a small value of c (Fig. 3). From Eq. (1) the α(300 K)≈ -600 μV/K in the virgin crystal reflects a small fraction ($c \approx 0.0009$) of Mn(II) ions, and thermal cycling to 1000 K in vacuum (10^{-3} torr) results in a small oxidation of the sample above 500 K giving a similarly small fraction of Mn(IV) ions.

(ii) *An abrupt drop in* $\alpha(T)$ *and* $\rho(T)$ *at* T_{JT} *to a nearly temperature-independent value for* $T > T_{JT}$. Reversibility of $\alpha(T)$ in subsequent runs indicates that the conductive state in the *O*-orthorhombic phase does not reflect a change in the oxidation state of the MnO_3 array. Instead of a small fraction of polarons participating in conduction, a large fraction of the *e* electrons appears to be involved even though the crystal is essentially single-valent Mn(III) and the *e* electrons remain strongly coupled to locally cooperative, dynamic Jahn-Teller deformations of the $MnO_{6/2}$ octahedra. A dynamic disproportionation reaction 2Mn(III)=Mn(IV)+Mn(II) would create mobile carriers, and a temperature-independent $\alpha(T)$ is characteristic of polaronic conduction. However, a temperature-independent $\rho(T)$ is not characteristic of polaronic conduction even for a motional enthalpy $\Delta H_m < kT$. On the other hand, a temperature-independent $\rho(T)$ is characteristic of a fixed mean free path for itinerant electrons. However, the value of $\rho(T)$is too high for conventional itinerant electrons with a mean free path of one lattice parameter; the mobility $\mu = e\tau_s/m^*$ must be reduced by an unusually heavy effective mass resulting from the strong electron-lattice coupling implicit in a dynamic Jahn-Teller stabilization. A large m^* would also reflect a nearly dispersionless $\varepsilon(\mathbf{k})$ curve, which in turn would give rise to a nearly temperature-independent thermoelectric power.

In order to check whether a change from an anisotropic antiferromagnetism to an isotropic ferromagnetism accompanies the change in transport properties at T_{JT}, we measured the paramagnetic susceptibility $\chi(T)$. Figure 4 shows that

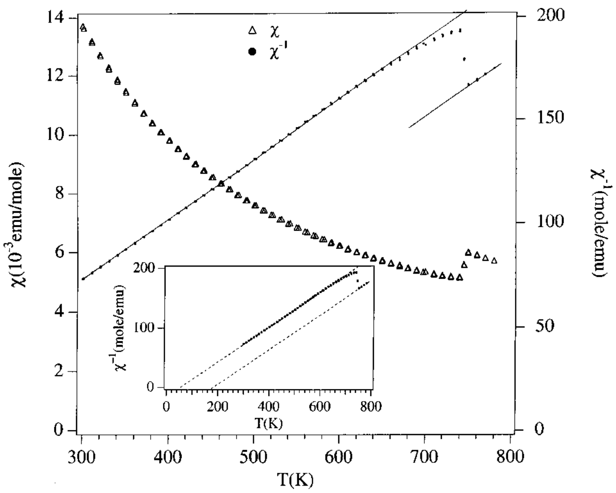

FIG. 4. Magnetic susceptibility $\chi(T)$and $\chi^{-1}(T)$ for single-crystal $LaMnO_3$. $\chi_\parallel$ and $\chi_\perp$could not be resolved in the paramagnetic O' phase, but they are resolved below T_N.

$\chi(T)$ follows precisely a Curie-Weiss law both below 650 K and above T_{JT} with the same Curie constant $C=3.41$ corresponding to a $\mu_{eff}=5.22\mu_B$. The significant change on crossing T_{JT} is an abrupt increase in the Weiss constant from θ=52 K for $300<T<650$ K to θ=177 K for $T>750$ K. The Weiss constant $\theta<T_N$ in the antiferromagnetic O' phase reflects the sum of a positive interaction in the (001) MnO_2 planes and a negative interaction along the c axis; in the O phase a $\theta>T_c$ reflects an isotropic ferromagnetic interaction that could be viewed as a superexchange interaction associated with locally cooperative, dynamic Jahn-Teller deformations that correlate occupied e orbitals on one side of an oxygen atom with empty e orbitals on the other.[6] However, the transport data indicate a real, not a virtual, charge transfer from occupied to empty e orbitals as in a double-exchange interaction. Moreover, the discontinuous increase in θ to a value $\theta>T_N=177$ K suggests a change in the character of the interatomic interactions. It seems that the double-exchange interaction in the O phase of single-valent $LaMnO_3$ can be neither that envisaged by Zener nor that by de Gennes. A full disproportionation reaction would give a spin only $\mu_{eff}=5.0\mu_B$, whereas it is $4.89\mu_B$ for localized Mn^{3+}. The appearance of charge disproportionation, which gives rise to a small change $\Delta\mu_{eff}=0.11\mu_B$, cannot be ruled out for the phase above T_{JT}.

In order to test a charge-disproportionation model further, we investigated the sensitivity of the magnetic interactions to the oxidation state of the MnO_3 array. An $x=0.025$ Ca-doped $LaMnO_3$ sample was prepared and $\rho(T)$, $\alpha(T)$, and $\chi(T)$were measured as for $LaMnO_3$. The $\alpha(T)$ and $\rho(T)$ data in the O phase above T_{JT} were essentially unchanged by the doping as were the θ and C values of the Curie-Weiss paramagnetism in both the O and O' phases. Only the transport properties of the polaronic O' phase and T_{JT} were changed; α(300 K)>0 dropped dramatically as expected from Eq. (1) and Fig. 3, and T_{JT} was lowered by about 50 K. Like $\chi(T)$, the transport properties in the O phase apparently depend on a large number of e electrons and remain insensitive to a 2.5% reduction.

In summary, the data show a transition at T_{JT} from polaronic conduction to a cooperative charge transfer of many heavy charge carriers. The orbital-ordering distortion is significantly reduced (Fig. 1), but there is no change in the mean ⟨Mn-O⟩ bond length or rotation of the $MnO_{6/2}$ octahedra. The Curie constant also remains unchanged, but the Weiss constant increases abruptly. In the polaronic phase below T_{JT}, the interatomic Mn-O-Mn spin-spin interactions can be treated by superexchange theory; in the conductive phase above T_{JT} a real charge transfer and isotropic ferromagnetic coupling suggest that a double-exchange model is appropriate. The electrons must move from filled to empty e orbitals that correspond to a partial charge disproportionation. The strong electron-lattice coupling that leads to a charge disproportionation gives them a heavy effective mass m^* and indicates a hybridization of electron and phonon states, making the charge carriers vibronic. A large Debye-Waller factor associated with the vibronic state above T_{JT} has been found by neutron diffraction.[10] The tunneling time of the electrons from one Mn atom to another is slowed to the period ω_O^{-1} of a cooperative oxygen-atom vibration, which means the mobile spins have time to become aligned with the localized spin on an individual atom, so the electron transfer integral becomes spin dependent as in the de Gennes model of double exchange. However, we would distinguish this vibronic picture of double exchange in a single-valent system from the de Gennes model of itinerant electrons in a mixed-valent array.

We have learned after submitting this manuscript that Gorkov and Kresin[11] have predicted a metallic ferromagnetism in $LaMnO_3$ above T_{JT} by their revised band calculation. However, the paramagnetic phase above T_{JT} with strong ferromagnetic coupling shows peculiar transport properties which are incompatible with a band electronic model.

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