Low-Temperature Permittivity of Insulating Perovskite Manganites

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Measurements of the low-frequency (f ≤ 100 kHz) permittivity (ε) and conductivity (σ) at T ≤ 150K are reported for La1−xCa2MnO3 (0 ≤ x ≤ 1) and Ca1−ySr2MnO3 (0 ≤ y ≤ 0.75) having antiferromagnetic, insulating ground states covering a broad range of Mn valencies from Mn3+ to Mn4+. Static dielectric constants are determined from the low-T limiting behavior. With increasing T, relaxation peaks associated with charge-carrier hopping are observed in the real part of the permittivities and analyzed to determine dopant binding energies. The data are consistent with a simple model of hydrogenic impurity levels and imply effective masses m*/m∞ ~ 3 for the Mn4+ compounds. Particularly interesting is a large dielectric constant (ε0 ~ 100) associated with the C-type antiferromagnetic state near the composition La0.2Ca0.8MnO3.

PACS numbers: 75.47.Lx, 75.50.Ee, 77.22.Ch, 77.22.Gm, 71.55.-i

I. INTRODUCTION

Recently, the lightly electron-doped manganites, e.g. Ca1−xLaxMnO3 (L is a Lanthanide), have been shown to exhibit a novel phase separated ground state, composed of distinct crystallographic and magnetic phases on a mesoscopic scale. Detailed neutron diffraction studies of Ca1−xLaxMnO3 (x ≤ 0.2) indicate that the heterogeneity of this system is intrinsic, associated with an extremely fine balance between competing ferromagnetic (FM) double-exchange and antiferromagnetic (AF) superexchange interactions.

This paper reports investigations of the compositional dependence of the static dielectric constant (ε0) in the Mn4+-rich portion of the manganite phase diagram, accessible through low-frequency (f ≤ 100 kHz) impedance measurements at low temperature (T ≥ 2 K). Very few studies of the permittivity of manganites have been reported. Specimens for which homogeneous, insulating ground states predominate are the particular focus: The A-type AF phase (LaMnO3), the Wigner-crystal AF phase (La1/3Ca2/3MnO3), the C-type AF phase (La0.2Ca0.8MnO3), and the G-type AF phase (Ca1−ySr2MnO3). In general, ε0 is an important parameter for models of phase separation involving the segregation of doped charge carriers on a mesoscopic scale, relevant for some compositions near to those investigated here. It is also a key parameter in determining polaronic binding energies. In addition, impedance measurements provide direct information about the charge carriers since carrier hopping yields a dipolar contribution to the permittivity.

II. EXPERIMENT

Polycrystalline La1−xCa2MnO3 (LCMO) and Ca1−ySr2MnO3 (CSMO) specimens were prepared by standard solid-state reaction; the preparation methods and magnetization and transport measurements are reported elsewhere. Powder x-ray diffraction revealed no secondary phases and iodometric titration, to measure the average Mn valence, indicates the oxygen content of all specimens falls within the range 3.00±0.01.

AC impedance measurements were conducted with an HP4263B LCR meter at frequencies f = 100 Hz, 120 Hz, 10 kHz, 20 kHz, 100 kHz using a 4-terminal pair arrangement. Reliable measurements of ε were restricted to T ≤ 160 K where the capacitive reactance was sufficient large (≥ 0.1Ω). Typical specimen dimensions were 3×1.0×0.5 mm. Silver paint electrodes were applied on the largest, polished faces of the specimens and annealed at 300°C for 2 h to improve contact resistance. Contact capacitance can lead to apparently large values of ε and thus some care is required to distinguish the true response of the sample. To rule out the influence of contacts, the impedances of several specimens were re-measured after further polishing to reduce the electrode spacing by at least a factor of two; in all cases the low-temperature data agreed within geometric uncertainties of ±10%. The results were also independent of applied DC bias from 0V-2V, and ac voltage in the range 50mV-1V.

III. RESULTS AND ANALYSIS

A. Relations

Quite generally, the complex dielectric permittivity of a solid, ε = ε' − iε", can be expressed as, ε = ε∞ + ε1 + εd. ε∞ is the high-frequency dielectric constant associated with displacements of ionic charge distributions relative to their nuclei. The lattice contribution, ε1, arises from displacements of ions and their charge distributions. εd represents a dipolar contribution, associated in the present materials with charge-carrier hopping. ε∞ and ε1 are generally frequency- and temperature-independent at low T. The frequency-dependent dipolar conductivity is described by a power law and is reflected in the
dielectric loss ($\varepsilon''$),

$$\sigma_d(\omega) = \sigma_0 \omega^s = \omega \varepsilon_0 \varepsilon''_d(\omega),$$

(1)

where $\omega(= 2\pi f)$ is the angular frequency, $\sigma_0$ is generally weakly $T$ dependent, $s \leq 1$, and $\varepsilon_0$ is the permittivity of free space. The dipolar contribution to the real part of the permittivity ($\varepsilon'_d$) has a characteristic frequency response that is related to that of $\sigma_d$ by the Kramers-Kronig relations,

$$\omega \varepsilon_0 \varepsilon'_d(\omega) = \sigma_d(\omega) \tan(s\pi/2).$$

(2)

Dipolar relaxation effects are often evidenced in $\varepsilon'_d$ or $\varepsilon''_d$ as maxima at a temperature that increases with increasing $f$. These features can be described empirically by the Cole-Cole expression,

$$\varepsilon_d = \varepsilon_{d,\infty} + \frac{\Delta \varepsilon_d}{1 + (i\omega\tau)^{1-\beta}},$$

(3)

where $\varepsilon_{d,\infty}$ is the value of $\varepsilon_d$ in the high-frequency limit, and $\Delta \varepsilon_d$ is the difference between low- and high-frequency limiting values. $\beta$ is an empirical parameter describing (symmetric) relaxation broadening ($\beta = 0$ corresponds to monodispersive relaxation), and $\tau$ is the relaxation time.

B. Temperature Dependence of Permittivity

$\varepsilon'(T)$ and $\sigma(T)$ are shown for the end-member compounds, LaMnO$_3$ (LMO) and CaMnO$_3$ (CMO) in Fig. 1. $\varepsilon'(T)$ is shown for LCMO ($x = 0.65, 0.70, 0.80$) and CSMO ($y = 0.1, 0.50$) in Fig. 2 and Fig. 3 respectively.

The data for most of the specimens exhibit the canonical behavior described in the preceding section; at the lowest temperatures, $\varepsilon'$ is independent of temperature and frequency, reflecting an intrinsic static dielectric constant, $\varepsilon_0 \equiv \varepsilon'(T \to 0)$. LMO [Fig. 1 (a)] has $\varepsilon_0 = 18$, in good agreement with values in the range 15–21 reported previously. In this low-temperature regime, the dc conductivity is small, and the dispersive dipolar conductivity is apparent [Fig. 1 (b)]. With increasing temperature, dispersive maxima develop in $\varepsilon'$, the signature of dipolar relaxation with a relaxation time $\tau$ that decreases with increasing $T$. Two sets of relaxation maxima are evident in the CMO data, the one at lower $T$ evident as a “shoulder” in the data for the range 40–60 K. The $\varepsilon'$ data for CMO and LCMO ($x = 0.80, 0.84$) do not reach this $T$-independent regime for $T \geq 2$ K, so $\varepsilon_0$ must be
evaluated by extrapolation. The data for CMO are near saturation: $\varepsilon_0 = 55 \pm 6$ is estimated from the average of the $T = 0$ extrapolated values of $\varepsilon'$ for $f = 10$ kHz, 20 kHz, 100 kHz. For $x = 0.80$ and 0.84 we employ a procedure that exploits the power-law frequency behavior for the dipolar terms as described in the next subsection.

Fig. 4 demonstrates that the dipolar contributions to $\varepsilon'$ and $\sigma$ have a common origin, consistent with charge-carrier hopping. In Fig. 4(a), linear least-squares fits of $\sigma_d$ vs. $f$ in a double logarithmic plot yield powers $s$ at various $T$’s for LaMnO$_3$. In Fig. 4(b) these values of $s$ and $\varepsilon'_d \equiv \varepsilon' - \varepsilon_0$ are used to verify Eq. 2.

Dipolar relaxation times, $\tau$, were determined for all compounds by fitting $\varepsilon' (\omega)$ at fixed temperatures to Eq. 3 as shown in Fig. 4(a) for LMO. Values of $\beta$ fell in the range 0.4–0.8, indicating a distribution of rates as is typical for hopping systems. $\tau$ is plotted against inverse temperature for both LMO and CMO in Fig. 4(b) (for CMO, data in the regime of overlap for the two relaxation peaks were excluded). $\tau(T)$ is approximately Arrhenius-like in the accessible temperature ranges, $\tau = \tau_0 \exp(U/k_B T)$. For several compounds, two activation energies, $U_1$ and $U_2$, are defined at high- and low-$T$ as observed for CMO.

The crossover between these two relaxation regimes coincides with a crossover in the $T$ dependence of the ac and dc resistivities [dashed curve in Fig. 4(b)]. This behavior is characteristic of a change in the conduction mechanism from thermal activation of carriers from impurity (dopant) levels to the conduction band at high $T$, to impurity-band conduction at low $T$. This crossover is detectable in $\tau$ only for specimens having a sufficient carrier density to yield a measurable dipolar contribution to $\varepsilon'$ extending to the low-$T$ regime. Values of activation energies and associated values of $\tau_0$ are listed in Table I for all compounds.

C. Compositional dependence of $\varepsilon_0$

To determine $\varepsilon_0$ for LCMO $x = 0.80$ and 0.84, we employ Eq. 1 and 2 which imply, $\varepsilon' = \varepsilon_0 + A \omega^{s-1}$ [$A = (\sigma_0/\varepsilon_0) \tan(s\pi/2)$ is independent of $\omega$]. Thus plots of $\varepsilon'$ vs. $\omega^{s-1}$ at fixed temperatures yield $\varepsilon_0$ as the common intercept (i.e., in the limit $\omega \rightarrow \infty$). At each temperature, $s$ is determined from the frequency dependence of $\sigma_d$ as in Fig. 4. This procedure is validated by appli-
cation to LMO [Fig. 6 (a)], using data at the same temperatures for which $s$ was determined in Fig. 4 (a). The intercepts yield $\varepsilon_0 = 19 \pm 2$, in good agreement with the value $\varepsilon_0 = 18$ established from the low-$T$ saturation of $\varepsilon'$ in Fig. 1. Fig. 6 (b) shows results for $x = 0.80$, which yield $\varepsilon_0 = 87 \pm 12$. A similar analysis gives $\varepsilon_0 = 92 \pm 13$ for $x = 0.84$. The compositional dependencies of $\varepsilon_0$ for both the LCMO and CSMO compounds are shown in Fig. 7 and Table I.

**IV. DISCUSSION**

It is evident from the data in Table I that for the LCMO compounds (excluding CMO), larger values of $\varepsilon_0$ are associated with smaller values of $U_1$. This suggests an interpretation within a simple model for hydrogenic impurity levels for which the binding energy of donor (or acceptor) levels, which we identify as $U_1$, should scale inversely with the square of the dielectric constant, $U_1 = (m^*/m_e)(1/\varepsilon_0^2) \times 13.6$ eV. Figure 6 demonstrates good agreement with this simple relation for these specimens with effective mass ratios in the range $m^*/m_e \approx 1 - 1.3$.

For the nominally Mn$^{4+}$ CSMO compounds, $\varepsilon_0$ and $U_1$ are independent of composition within uncertainties.

Using the average of these values for the five CSMO compounds in the hydrogenic impurity expression implies $m^*/m \approx 3.2$. CMO, also nominally Mn$^{4+}$, appears to be an outlier. However, there is evidence that the CMO specimen has a higher carrier density than the CSMO compounds: both its higher low-$T$ conduc-
ity (the CSMO compounds have conductivities similar to that of LMO) and non-saturating $\varepsilon'$ (Fig. 1). Hall coefficient measurements on a similar CMO specimen yield an electron-like Hall number at room temperature, $n_H \approx 2 \times 10^{-4}$ f.u. $^{-1} \approx 3 \times 10^{18}$ cm$^{-3}$. A small oxygen vacancy concentration is a likely source of electrons, but a distribution of donors and acceptors is common in oxides. A smaller concentration of acceptors in the present compounds is expected to arise from several ppm levels of impurities (e.g., Al, Zn) in the starting chemicals. Assuming this value of $n_H$ corresponds to full ionization of impurities, we have $N_D - N_A = n_H$ where $N_D$ and $N_A$ are the donor and acceptor concentrations, respectively. Donors (or acceptors) with bound electrons enhance the polarizability of a host lattice, and can plausibly account for the larger value of $\varepsilon_0$ observed for CMO. At low carrier density, where the donor-doped dielectric constant is not much larger than that of the undoped host ($\varepsilon_h$), $\varepsilon - \varepsilon_h = 4\pi N_D \alpha$, where $\alpha$ is the polarizability of a single donor. Taking $\varepsilon_h = 36$ (the average value for the CSMO specimens) and $N_D = n_H$ yields the reasonable value, $\alpha = 3.8 \times 10^{-19}$ cm$^3$.

Perhaps the most interesting results of the present work are the very large values of $\varepsilon_0$ observed for the two LCMO compounds, $x = 0.80$ and $0.84$ [Fig. 7 (a)]. Recent neutron diffraction studies on specimens with these same compositions$^{16}$ indicate a mixture of monoclinic and orthorhombic structures at low $T$ associated with C-type AF and Wigner-crystal (WC) type$^{15,16}$ Jahn-Teller distorted, charge- and orbitally-ordered states, respectively. Both specimens contain approximately 80% of the C-type phase. The implication is that the large values of $\varepsilon_0$ are associated with the monoclinic, C-type AF phase. Taking the value $\varepsilon_0 \approx 31$ as representative of the WC phase (optimized near $x = 2/3$)$^{15,16}$, and assuming measured values of $\varepsilon_0$ for $x = 0.8$ and $0.84$ represent weighted averages (by volume) of the values of the two component phases, a pristine C-type polycrystal is predicted to possess an even larger, $\varepsilon_0 \sim 105$. The increase of $\varepsilon_0$ in going from $x = 0.65$ to $x = 0.7$ suggests that the $x = 0.7$ specimen contains $\sim 10$% of the C-type monoclinic phase. A much smaller component of the C-type phase was also detected in structural studies on a $x = 2/3$ compound$^{16}$.

In the absence of any known structural features (e.g., off-center atoms) that could enhance $\varepsilon_0$ of the C-type phase over that of the WC phase, the substantially lower values of $\varepsilon_0$ observed for compositions $x = 0.65$ and $0.70$ suggest that the one-dimensional charge/orbital ordering that characterizes the C-type phase may play a role in determining the larger $\varepsilon_0$ found for $x = 0.8$ and $0.84$. It is well-established from work on heavily doped Sr$^{12}$ and La$_2$CuO$_{4+x}$,$^{19}$ that enhancements in $\varepsilon_0$ by more than an order of magnitude above undoped, host-lattice values are associated with the polarizability of donors or acceptors with bound charges. The results for the latter material may be particularly relevant here because they demonstrate that, in a related class of AF oxides, this impurity-state polarizability enhancement follows the electronic anisotropy. The C-type AF state is highly anisotropic, with FM double-exchange interactions mediating a substantially higher carrier hopping rate along the direction of $d_{3z^2-r^2}$ orbital polarization, and superexchange interactions suppressing hopping in the transverse directions. It is plausible that the La-donor polarizability is correspondingly anisotropic. Thus the large $\varepsilon_0$ found for the $x = 0.8$ and $0.84$ polycrystals could arise primarily from an enhancement of $\varepsilon_0$ along (||) the FM chains of the C-type phase [the (101) direction of the monoclinic structure], with $\varepsilon_0$ in the transverse (⊥) directions comparable to that of the WC phase. Within this scenario, the inferred $\varepsilon_0 \sim 100$ for a C-type polycrystal would represent an average, $\sim (\varepsilon_0 || \varepsilon_0 ⊥)^{1/2}$, such that $\varepsilon_0 || \sim 300$. To our knowledge single crystals of the C-type compositions have not been reported, but it is clear that a study of the anisotropy of $\varepsilon_0$ in such materials would provide further insight into the role of the orbital order in enhancing $\varepsilon_0$.

V. ACKNOWLEDGMENTS

The work at the University of Miami was supported by NSF Grant No. DMR-0072276 and at Montana State University by NSF Grant No. DMR-0301166.

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