Correlations between the magnetic and structural properties of Ca-doped BiMnO$_3$

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The Bi$_{1-x}$Ca$_x$MnO$_3$ system is known to exhibit charge ordering for a much broader range of $x$ than the La$_{1-x}$Ca$_x$MnO$_3$ system. However, the properties of Bi$_{1-x}$Ca$_x$MnO$_3$ over the entire doping range are not well understood. We have performed magnetization and resistivity measurements as well as x-ray absorption and x-ray diffraction measurements on Bi$_{1-x}$Ca$_x$MnO$_3$ to correlate structural, magnetic, and transport properties. The system is insulating and antiferromagnetic for the entire range of $x$ studied ($x \geq 0.4$) except near $x \approx 0.9$, where we find a canted spin arrangement with approximately one Bohr magneton per Mn site. Detailed magnetization measurements were performed as a function of field and temperature to explore the net moment on the Mn sites as a function of $x$ and reveal the charge ordering and Néel temperatures. X-ray absorption measurements reveal significant structural distortions of the Mn-O bond distributions with increasing Bi content that correlates directly with increasing charge-ordering temperatures. Moreover, the x-ray diffraction data reveal peak splittings consistent with lower-symmetry cells as Bi content increases. These structural-magnetic correlations point to the importance of Mn-O distortions in stabilizing the charge-ordered state in the manganites.

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I. INTRODUCTION

As a function of temperature, pressure, doping, and $A^{3+}/A^{2+}$-site ionic radius, perovskite mixed-valent manganites $A_1^{3+}A_x^{2+}$MnO$_3$ (e.g., $A^{3+} = $ Bi, La, Pr, Nd, etc. and $A^{2+} = $ Ca, Sr, Ba, Pb, etc.) show intriguing properties such as structural transformations, charge ordering (CO), metal-insulator transitions, and magnetic ordering [ferromagnetic (FM)-antiferromagnetic (AF)] transformations. 1-4 In addition to the rich basic physics exhibited by these materials, there is also much interest from the technological perspective in these materials because they are known to exhibit “colossal” magnetoresistance (CMR). 5, 8

The phase diagram of the prototypical La$_{1-x}$Ca$_x$MnO$_3$ (LCMO) system is well documented, and extensive structural, magnetic, and transport measurements have been performed. 1, 9 For $0 < x < 0.21$, the system is an insulator (I) with a canted antiferromagnetic (CAF) or ferromagnetic ground state. For the range $0.21 < x < 0.5$, a ferromagnetic metallic (FM) ground state occurs that undergoes a coincident metal-to-insulator (MI) and FM-to-paramagnetic (PM) transformation on the temperature scale $150-250$ K. 2, 6, 7 In the $0.50 < x < 0.875$ region, the materials are insulators with a charge/orbital-ordered (CO ordered) and AF-ordered ground state, which, upon elevating the temperature, first loses its AF ordering (at $T_N$) and then, at a higher temperature ($T_{CO}$), its CO ordering. 8

Bi$_{1-x}$Ca$_x$MnO$_3$ (BCMO) constitutes a very interesting but less-studied system. Early experiments showed that the system is insulating over a broad region of Ca doping $0.2 < x < 1.0$. 10 In addition, strong charge ordering has been observed in neutron-scattering measurements for $x \approx 0.8$. 4, 14 The $x = 0$ end member was found to be ferromagnetic with a moment per Mn approaching the theoretical maximum. These intriguing properties, contrasted with those of the LCMO system, make this system ideal for understanding the correlations between structure, transport, and magnetic properties in manganese materials.

In this work we first draw together structural, magnetic, and resistivity results, both from the literature and from work in our group, into an overall phase diagram for the BCMO system for $0.4 < x < 1.0$. We then focus on systematic x-ray absorption spectroscopy (XAS) measurements of the BCMO materials. Despite substantial disparities with other more-studied systems, the continuous Bi-induced stabilization of the Mn$^{3+}$ state is demonstrated with Mn-K near-edge XAS measurements. Both near-edge and extended x-ray absorption fine-structure (EXAFS) XAS measurements provide direct evidence of significant local distortions accompanying increasing Bi content in this system.

II. PREVIOUS WORK ON Bi$_{1-x}$Ca$_x$MnO$_3$

A large, but somewhat scattered, body of work has been performed on the doped BCMO system. This work is summarized in this section. Bokov, Grigoryan, and Bryzhina 10 studied the structural, magnetic, and resistivity properties of the BCMO system for $0.2 < x < 1.0$. Their phases included two monoclinic phases and one orthorhombic phase as a function of temperature for $x < 0.4$; one of the monoclinic phases disappears for $x > 0.4$, for $0.4 < x < 0.83$ a high-temperature cubic phase transforms to a monoclinic low-temperature phase, and above $x > 0.83$ the more distorted monoclinic phase gives rise to a higher-symmetry orthorhombic phase. Their magnetic measurements showed a FM-like Curie constant ($\theta$) at
high temperatures for all \( x < 0.9 \).

Chiba et al.\textsuperscript{11,13} contrasted the magnetic, electrical, and magnetoresistance properties of \((\text{Bi},\text{AE})\text{MnO}_3\) (\(\text{AE} = \text{Ca}, \text{Sr}\)) with those of LCMO in the highly doped \( x \approx 0.8 \) regime. They noted that while the Bi- and Ca-based systems had the same crystal symmetry and weak ferromagnetism in this Ca-rich region, the magnetic moments in the Bi system were larger than those in the La system at the same Ca content. CaMnO\(_3\) was found to exhibit semiconductor-type and antiferromagnetic behavior.\textsuperscript{12} Chiba et al.\textsuperscript{11} found that the low-temperature resistivity drops continuously when CaMnO\(_3\) is doped with Bi\(^{3+}\) (electron doping) and reaches minimum resistivity at \( x = 0.875 \) with a weak temperature dependence. At \( x = 0.85 \) (also \( x = 0.8 \)), a sharp increase in magnetization with increasing temperature was found, which suggests anomalous magnetic transition temperatures. The Néel temperature was found to be almost constant for \( 0.875 \leq x \leq 0.95 \), while the paramagnetic Curie temperature decreased with increasing Ca doping. At \( x = 0.875 \), the Néel temperature approaches the paramagnetic Curie temperature and a maximum saturation magnetization of \( 1.1 \mu_B \) per Mn site is obtained—this is about \( \frac{1}{2} \) of the fully aligned value of \( 3.1 \mu_B \), suggesting spin canting.

Cheong and Hwang expanded on the magnetic phase diagram of Chiba et al.\textsuperscript{11} by studying the charge-ordered phases for \( 0.5 < x < 0.7 \).\textsuperscript{9} For this range, the charge-ordering temperature is always above 300 K. The maximum charge-ordering temperature of 332 K was found to occur at \( x \approx 0.63 \); the same behavior of the charge-ordering temperature was observed in the LCMO system.

Bao et al.\textsuperscript{4} performed neutron-scattering, electron-diffraction, and bulk magnetic measurements on single-crystal BCMO (0.74\( \leq x \leq 0.82 \)). For \( x = 0.82 \), a structural transition was found at the charge-ordering temperature \( T_{\text{CO}} = 210 \text{ K} \) in which the lattice parameters changed abruptly. This coincides with the transition from orthorhombic to monoclinic \( I \) found by Bokov, Grigoryan, and Bryzhina.\textsuperscript{10} Above \( T_{\text{CO}} \), ferromagnetic spin fluctuations were found by neutron diffraction. These fluctuations switch over to antiferromagnetic fluctuations below \( T_{\text{CO}} \). Strong competition between FM double-exchange charge ordering and AF superexchange occurs in this system. The Néel temperature was found to be 160 K. The same trends were also found in earlier neutron-diffraction measurements by Turkевич and Plakhtii\textsuperscript{14} on Bi\(_{0.15}\)Ca\(_{0.85}\)MnO\(_3\). They found the signature of the onset of antiferromagnetic Mn-Mn interactions at low temperatures as evidenced by appearance of \{110\} and \{211\} superstructure lines.

Optical conductivity measurements by Liu, Cooper, and Cheong\textsuperscript{15} divide the phase diagram of this system into three distinct temperature regions. For \( T > T_{\text{CO}} \) ferromagnetic correlations exist, for \( T_N < T < T_{\text{CO}} \) phase separation into CO-(AF) and ferromagnetic regions coexists, and for \( T < T_N \) a charge gap develops, and a long-range antiferromagnetism is observed.

Murakami et al.\textsuperscript{16} found evidence for charge ordering in Bi\(_{0.5}\)Ca\(_{0.5}\)MnO\(_3\) coconitmant with 32- and 36-fold periodicity. The charge-ordering temperature \( T_{\text{CO}} \) was found to be \( \approx 160 \text{ K} \) and below \( T_{\text{CO}} \), the magnetic structure was transformed from a paramagnetic to an antiferromagnetic phase. Long-period structures with 32- and 36-fold periodicity associated with charge ordering in Bi\(_{0.5}\)Ca\(_{0.5}\)MnO\(_3\) were found.

Utilizing high-pressure synthesis, Sugawara and Lida\textsuperscript{17} obtained the end member BiMnO\(_3\). It was found that unlike LaMnO\(_3\), BiMnO\(_3\) is ferromagnetic with a Curie temperature of 103 K. The saturation magnetization was observed to be \( \approx 4 \mu_B \) per Mn site. A distorted perovskite structure with a triclinic pseudocell unit was found.

Recently, Atou et al.\textsuperscript{18} reported powder-neutron-diffraction measurements of the structure of the ferromagnetic perovskite BiMnO\(_3\) formed under high pressure. A distorted perovskite structure was found with monoclinic C\(_2\) space-group symmetry. They suggested that the distortions were caused by the polarized Bi-6\(_s\) lone pairs.\textsuperscript{19} The combined Jahn-Teller instability of Mn\(^{3+}\) and lone pair-induced distortions result in a highly disordered BiMnO\(_3\) system with a range of Mn-O bonds between 1.78 and 2.32 Å. The origin of the ferromagnetic tendency is uncertain.

Recently, Ohshima et al.\textsuperscript{20} prepared films of BiMnO\(_3\) on SrTiO\(_3\) substrates. Although the films (200–1200 Å) exhibited the ferromagnetic behavior seen in the corresponding bulk material, the saturation moment of the thick films fell short (\( M = 2.8 \mu_B \)) of the bulk value (\( M = 3.6 \mu_B \)). In addition, a strong dependence of the saturation moment on film thickness was found. Also, unlike the bulk material, strong hysteresis was found in the film samples.

The broad array of interesting properties suggests a deep correlation between the long-range and local structure, and the magnetic and transport trends in the BCMO system.

### III. Experimental Methods

We have prepared a series of BCMO (\( x \geq 0.4 \)) polycrystalline samples using the standard solid-state reaction method. Stoichiometric mixtures of Bi\(_2\)O\(_3\), CaCO\(_3\), and MnO\(_2\) were mixed, ground, and pressed into pellets, which were calcined at 900 °C. After calcination, the samples were reground and sintered at 1000 °C in air. This was repeated one more time. BiMnO\(_3\) was synthesized under high pressure (25 kbar) at 800 °C by using a cylinder-piston-type pressure furnace. The purity of BiMnO\(_3\) was checked by x-ray fluorescence spectroscopy.

Magnetization, resistivity, x-ray diffraction, and x-ray absorption measurements were performed. Magnetic measurements were performed using a superconducting quantum-interference device magnetometer. The standard four-probe method was used for resistivity measurement. X-ray diffraction (XRD) measurements were carried out using a x-ray diffractometer with a liquid-nitrogen-cooled Li-drifted germanium detector and Cu-K\(_\alpha\) radiation. Lattice parameters were extracted using DICHOL and ITO software packages.\textsuperscript{21} X-ray-absorption spectra were measured at Brookhaven National Laboratory’s National Synchrotron Light Source beam lines X11A, X18B, X19A, and X23A2. Si(111) monochromator crystals were used on X18B and X19A while Si(311) crystals were used on X23A2. Spectra were taken in...
transmission mode using \( \text{N}_2 \)-filled ion chambers. The reduction of the x-ray absorption measurements was performed using standard procedures.\(^{23} \) Calibration was accomplished by defining the first inflection point in a simultaneous Mn foil as 6539 eV, the ionization threshold. Consistency between different beamlines was checked by using a MnO\(_2\)-powder reference sample over the complete data range. The background and signal extraction was carried out using AUTOBK.\(^{23} \) The fine-structure signals were extracted from the spectra as the difference between the normalized spectra and an adjustable spline function fit through the post-edge region normalized by the absorbance decrease with energy, the parameters of which were adjusted to minimize low-frequency residuals in the Fourier transform. After comparison, two to ten individual scans were averaged. Representative data are given in the inset in Fig. 10. Information about the Mn-O bond distributions was obtained by fitting the \( k^3 \) weighted raw data over the range \( 2 < k < 12.3 \) Å\(^{-1} \) \( \{ k = \sqrt{(2m/\hbar^2)(E-E_0)} \} \). Fitting was made using the functional form

\[
\chi_{\text{model}}(k) = \sum_i S_i^2 \frac{N_i}{k R_i^2} f_i(\pi, k, R_i)\exp\left(-2\sigma_i^2 k^2 + \frac{2}{3} C_4 k^4\right) \times \sin[2kR_i - \frac{4}{3} C_3 R_i^3 + \phi_i(\pi, k, R_i)],
\]

(1)

where \( S_i^2 \) is the scale factor for the multielectron effects, \( N_i \) is the coordination number of the \( i \) shell, \( R_i \) is the radius of the \( i \) shell, \( \sigma_i^2 \) is the mean-square radial displacement or Debye-Waller factor, \( f_i \) is the backscattering amplitude of the photoelectron due to the atoms of the \( i \) coordination shell, \( C_3 \) and \( C_4 \) are cumulants\(^{24,25} \) of a distribution to model anharmonic effects and/or non-Gaussian disorder,\(^{25,26} \) respectively, and \( \phi_i \) is the phase shift.

The inhomogeneously broadened (fine structure) \( \chi \) based on the statistical ensemble of scattering path lengths\(^{27} \) is written as

\[
\langle \chi(k;R) \rangle = \int dR P(R) \chi(k;R).
\]

(2)

In the cumulant approach to distributions one represents the Fourier transform of a distribution by its moments. For small deviations from a Gaussian distribution a rapidly converging series makes possible a description by a small number of parameters. For the effective distribution we have

\[
\ln \int_0^\infty P(r,\lambda) e^{2ikr} \, dr = C_0 + \sum_{n=1}^\infty \frac{(2ik)^n}{n!} C_n, \quad (3)
\]

where

\[
P(r,\lambda) = \rho(r) e^{-2r/\lambda \rho^2}.
\]

The leading cumulants \( C_n \) are

\[
C_1 = \langle R \rangle,
\]

\[
C_2 = \sigma^2 = \langle R^2 \rangle - \langle R \rangle^2,
\]

\[
C_3 = \langle R^3 \rangle - 3\langle R^2 \rangle \langle R \rangle + 2\langle R \rangle^3,
\]

\[
C_4 = \langle R^4 \rangle - 4\langle R^3 \rangle \langle R \rangle - 3\langle R^2 \rangle^2 + 12\langle R^2 \rangle \langle R \rangle^2 - 6\langle R \rangle^4. \quad (4)
\]

For an effective Gaussian distribution, cumulants \( C_n \) higher than the second vanish. In a convergent series the \( C_3 \) and \( C_4 \) parameters are related to asymmetry and flatness of the distribution, respectively [see Eq. (4)]. We performed fits with parameters up to \( C_4 \). Photoelectron scattering factors utilized in these fits were obtained using the code FEFF.\(^{28} \) These complex phase shifts included the electron damping. By defining the coordination numbers \( N \) as the values known for perovskite systems, average bond lengths \( R \) and Debye-Waller factors \( \sigma \) were extracted from the fits as well as \( C_3 \) and \( C_4 \) for the Mn-O (first-shell) bond distribution. The errors in these parameters were estimated based on the statistical spread found for fits to individual scans.

### IV. RESULTS AND DISCUSSION

#### A. X-ray-diffraction measurements

Figure 1 shows representative room-temperature x-ray diffraction profiles for the \( x = 0.4 \) and 0.9 materials. The \( x = 0.9 \) material was indexed with the orthorhombic \( (\alpha = \beta = \gamma = 90^\circ) \) perovskite structure and the extracted lattice parameters were \( a = 5.314, b = 7.480, \) and \( c = 5.297 \) Å. On the...
other hand, the $x=0.4$ pattern was indexed with a triclinic (nearly monoclinic) cell with the structural parameters of $a=3.848$, $b=7.655$, and $c=3.855$ Å. $\alpha=90.166$, $\beta=90.877$, and $\gamma=89.997^\circ$. This is consistent with the splitting of the $a$, $b$, and $c$ lattice parameters founded by Bokov, Grigoryan, and Bryzhina.\textsuperscript{10} The $x=0.6$ exhibited a similar triclinic structure but with the triclinic splittings much reduced. The $x=0.8$ assumes a structure with lattice parameters similar to that for $x=0.9$. Hence, reduced Ca content coincides with reduced space-group symmetry.

### B. Resistivity measurements

We performed resistivity measurements for $x=0.4$, 0.6, 0.8, and 0.9 (see Fig. 2, top panel). The BCMO system is insulating for $x \geq 0.4$ except near $x=0.9$. We noticed that the resistivity curves jump at the charge-ordering temperatures ($T_{CO}$) at 315, 330, and 190 K for $x=0.4$, 0.6, and 0.8, respectively. At the Néel temperature the $x=0.4$ sample shows a little dip indicating phase transition.

Zeng, Greenblatt, and Croft\textsuperscript{29} have reported an activated variation of the resistivity [$\rho = \rho_0 e^{\gamma/T}$] with $T_0 = 778$ K and $\rho_0 = 12.3 \, \Omega \, \text{cm}$ for CaMnO$_3$. In the bottom of Fig. 2 we compare the logarithmic resistivity variation for the $x=0.9$, BCMO material plotted versus $(1/T)$ and $(1/T)^{1/4}$. Unlike the pure $x=0.0$ system, the strong curvature of the $x=0.9$ material in the $1/T$ plot indicates that (i) its resistivity cannot be characterized as activated, and (ii) a simple crossover between two activation regions appears untenable. On the other hand the $(1/T)^{1/4}$ plot manifests a wide range of high-temperature linearity crossing over rather sharply to a low-temperature linear range. Fitting the data to the form [$\rho = \rho_0 \exp(T_0/T)^{1/4}$] yields $T_0$ and $\rho_0$ values of 1.42 MK and 1.19 $\mu\Omega$ cm at higher temperatures and 5470 K and 0.0136 $\Omega$ cm at lower temperatures.

As discussed below, at high temperatures these doped manganites manifest FM correlations. Models of these materials picture the FM correlations as local polarons randomly distributed and fluctuating.\textsuperscript{1} In this picture, the carrier hopping between FM fluctuations would involve disordered and potentially variable range hopping. In view of this, Fontcuberta \textit{et al.}\textsuperscript{30} used the $(T_0/T)^{1/4}$ dependence of the log of the resistivity data to characterize manganite system results. Varma\textsuperscript{31} argued in favor of a $(T_0/T)^{1/2}$-type behavior for manganite systems due to the importance of electron interactions in the localization. This provides some motivation for trying the three-dimensional variable range hopping form [$\rho = \rho_0 \exp(T_0/T)^{1/4}$] as an ansatz for plotting the data. At this juncture, however, we prefer to view the $(1/T)^{1/4}$ display of the data simply as an empirically useful method of characterizing the high-temperature variation of the resistivity.

In Fig. 2 (upper panel) the logarithmic variation of the resistivities of the $x=0.4$, 0.6, 0.8, and 0.9 materials is plotted versus $(1/T)$ and $(1/T)^{1/4}$. In the smaller range of this plot the $x=0.9$ variation is quite linear. The $x=0.4$, 0.6, and 0.8 material resistivities can also be well approximated by a [$\rho = \rho_0 \exp(T_0/T)^{1/4}$] form for $T > T_{CO}$ (the charge/orbital-ordering temperatures). For the high-temperature-region materials the values of $\rho_0$ and $T_0$ are given by 3.3 $\Omega$ cm, and 53 MK at $x=0.4$; 0.30 $\Omega$ cm, and 43 mK at $x=0.6$; 176 $\mu\Omega$ cm and 0.15 mK at $x=0.8$. The onset of the charge-ordered phase is characterized by a clear increase in the resistivity for all of the materials (see top of Fig. 2). This is consistent with the suppression of the carrier hopping associated with the charge-ordered phase. No clear resistivity anomalies associated with the AF-ordering temperatures ($T_N$) were observed.

It is worth noting for later reference that the magnitude of the resistivity at 300 K versus composition [see Fig. 3(b)] from our and previous work\textsuperscript{11} shows a distinctive dip (of nearly 2.5 orders of magnitude) in the $0.8<x<0.95$ range. A similar drop in the localization energy-scale parameters ($T_0$) is evident from our data. The low-$x$ side of this dip is associated with the suppression of CO correlations whereas the rise, approaching CaMnO$_3$, is related to the crossover to insulating behavior with the disappearance of doped carriers.
C. Magnetic measurements

Magnetization measurements [see Figs. 4(a)–(d)] were performed with magnetic fields of 1, 2, and 4 T for $x = 0.4$, 0.6, and 0.8, and 0.01, 0.1, and 1 T for $x = 0.9$. The magnetic susceptibility at the high temperatures showed Curie-Weiss-type behavior $[\chi = C/(T + \theta)]$ with an FM-like (i.e., negative) $\theta$ value over the $0.4 < x < 0.95$ as illustrated in Fig. 3(a). Here the Curie-Weiss behavior is for temperatures above the charge-ordering and antiferromagnetic transition temperatures. Thus this high-temperature range appears to be dominated by local ferromagnetic fluctuations (FMF) that are presumably mediated by Mn$^{3+}$/Mn$^{4+}$ hopping-induced double exchange interactions. With decreasing temperature our $x = 0.4$, 0.6, and 0.8 magnetization curves [see Figs. 4(a)–(d)]
exhibit distinct maxima at the charge-ordering temperatures ($T_{\text{CO}}$) indicated. The neutron-scattering results of Bao et al.\textsuperscript{4} and Turkovich and Plakhtii\textsuperscript{14} (on an $x=0.82$ material) have nicely correlated such maxima with the suppression of the FMF when the charge ordering freezes out the hopping mechanism. In the charge-ordered phase, AF superexchange interactions dominate,\textsuperscript{3} leading to an AF ordering at a temperature ($T_N$) in the 129–171 K range. $T_N$ is identified with a lower-temperature local-magnetization maximum. In the $x=0.8$ material the signature of the AF ordering is perceptible only as a subtle shoulder on the low-temperature side of the CO-related peak in the magnetization [see Fig. 4(c)].

The CO phase is suppressed for $x$ values above ~0.85. Our $x=0.9$ magnetization curves, for example, reflect the development of a robust net moment, which depends on the field strength, below a magnetic ordering temperature near 110 K. The onset of an AF-type order in this temperature range is common to materials with 0.85 $< x < 1.0$ in this system as is the appearance of a net FM moment in a magnetic field. This FM moment has been attributed in the past to FM-interaction induced moment canting. However the magnitude and nonlinear field onset of the FM moment varies strongly in this 0.85 $< x < 1.0$ range as illustrated by the $H = 1$ T moment variation vs $x$ (from our and other work) in Fig. 3(b).\textsuperscript{11} The rapid rise in the FM moment as $x$ increases through 0.85 marks the exit from the CO-AF state. The similar rapid magnetization drop near $x=0.95$ correlates with the suppression of a FM-$\theta$ value (high-$T$ FMF) in the same range. As has been noted previously, the $\theta$ value of the $x=1.0$ material is several folds larger than the AF-$T_N$, suggesting possible low-energy-scale nonmagnetic (covalency) effects in the pure Ca material.

The nonlinear field dependence of the magnetization in CaMnO$_3$ and its response to electron doping has been touched upon (although too briefly) in the literature. The roles of magnetic frustration, AF-domain-spin canting,\textsuperscript{29} homogeneous canted antiferromagnetic (CAF) order, and (most recently) local-scale FM/AF coexistence have all been brought up in this regard.\textsuperscript{29,32} In Fig. 5 we illustrate a subtle field-dependent behavior in these BCMO materials that may reflect a competing FM component in the CO-AF state of this system.

The $M/H$ curves in Fig. 5 represent the finite field susceptibility (as opposed to the differential susceptibility $dM/dH$) and help to highlight field-dependent saturation effects in the magnetic response. For the $x=0.9$ material [Fig. 5(d)] the $M/H$ curves at low field (e.g., $H=0.1$ T) manifest a tremendous response at the ordering temperature. The $H = 1$ T, $M/H$ curve shows a typical FM component response below $T_N$ and its smaller magnitude simply indicates that the FM response saturated at a much smaller field. This type of behavior is the basis for CAF or locally coexisting FM-AF order proposed for such $x>0.85$ range materials.

In a simple AF system, where the field energy is much less than $T_N$, the field response should be small and $M/H$ would be expected to increase with increasing field (at least until spin-flop effects saturate). The $M/H$ curves of the $x=0.4$ material in Fig. 5(a) illustrate this type of behavior.

In Fig. 5(c) the $M/H$ curves within the CO-AF phase of the $x=0.8$ material are shown. There is a small but clear nonlinear field response below about 100–120 K in the 1 T curve that is saturated in the higher-field curves. Comparison of Figs. 5(c) and (d) shows that this field effect in the $x=0.8$ material is similar in thermal variation, although much smaller in magnitude, to that in the $x=0.9$ material. Again in the $M/H$ results for $x=0.6$ (Fig. 5) a similar (albeit quite small) low-$T$ low-field increase in the response can be seen. For $x=0.6$ the energy scale for this effect has moved down to about 50 K. If one refers to the 1 T susceptibility results of Chiba et al.,\textsuperscript{11} one notes the presence of low-temperature FM-moment response in the $x=0.8$ and 0.85 materials in their CO/AF states. Whether these effects are related to local composition fluctuations, CO/AF-domain interface, or FM-like impurity site effects are at present unclear and further work on these effects is warranted.

D. Phase diagram

In Fig. 3 we summarize our results and previous magnetic results for the BCMO system as a phase diagram. Here the

![Figure 5](image_url)
previous work on this system focused either on restricted temperature or composition ranges. Our results augment the previous work and we have carefully attempted to draw together both our and previous results. The high-temperature phase is a paramagnet (PM) with ferromagnetic fluctuations (FMF) for the range $x<0.95$. The loss of FM correlations, approaching the $x=1.0$ (pure-Ca) material is marked by a dotted line. For the $x<0.85$ range the Mn$^{3+}$/Mn$^{4+}$ hopping, supporting the FMF, is quenched upon crossing a line of charge-ordering transitions (TCO). With further cooling, in the $x<0.85$ range, a transformation to an antiferromagnetic (while still CO ordered) ground state occurs below a line of temperatures $T_N$ (in the 110–160 K range).

It is worth noting that the charge-ordered phase of this system is stable over a wider range of compositions and temperatures than in any of the other manganite systems. In the case of the LCMO system, for example, in the $0.4< x<0.5$ range an FM metallic phase has replaced the charge-ordering state found here as the ground state. Moreover, in none of the other systems does the CO ordered state persist above room temperature. The loss of CO correlations for $x>0.8$ appears to enable the Mn$^{3+}$/Mn$^{4+}$ hopping and FMF to persist to room temperature, as evidenced by a wider FM Curie-Weiss range for the susceptibility and the strongly reduced resistivity in this $x$ range. Moreover, an FM component (peaking near $x=0.875$) also appears to be incorporated into the AF ground state in this range as reflected by the magnetization at 10-K variation versus $x$ in Fig. 3(c).

E. Mn-K near-edge XAS

Previous work has shown the Mn-K near-edge spectra to be useful in chronicling the Mn-valence/configuration change in the LCMO system. The Mn-K near-edge spectra for the extensively studied La$_{1-x}$Ca$_x$MnO$_3$ system, for $x=0.0$, 0.5, and 1.0.

The Mn-K near-edge XAS

Previous work has shown the Mn-K near-edge spectra to be useful in chronicling the Mn-valence/configuration change in the LCMO system. In Fig. 6 the main-edge (and pre-edge in the inset) spectra for $x=0.0$, 0.5, and 1.0 in this range an FM metallic phase has replaced the charge-ordering state.34 With further cooling, in the $x<0.85$ range, a transformation to an antiferromagnetic (while still CO ordered) ground state occurs below a line of temperatures $T_N$ (in the 110–160 K range).

It is worth noting that the charge-ordered phase of this system is stable over a wider range of compositions and temperatures than in any of the other manganite systems. In the case of the LCMO system, for example, in the $0.4< x<0.5$ range an FM metallic phase has replaced the charge-ordering state found here as the ground state. Moreover, in none of the other systems does the CO ordered state persist above room temperature. The loss of CO correlations for $x>0.8$ appears to enable the Mn$^{3+}$/Mn$^{4+}$ hopping and FMF to persist to room temperature, as evidenced by a wider FM Curie-Weiss range for the susceptibility and the strongly reduced resistivity in this $x$ range. Moreover, an FM component (peaking near $x=0.875$) also appears to be incorporated into the AF ground state in this range as reflected by the magnetization at 10-K variation versus $x$ in Fig. 3(c).

The Mn-K near-edge XAS

Previous work has shown the Mn-K near-edge spectra to be useful in chronicling the Mn-valence/configuration change in the LCMO system.29 In Fig. 6 the main-edge (and pre-edge in the inset) spectra for $x=0.0$, 0.5, and 1.0 in this system are shown. It should be noted that the peak feature $B$ shifts markedly between the formally Mn$^{3+}$ and Mn$^{4+}$ compounds with $x=0.0$ and 1.0; the $x=0.5$ material has an intermediate chemical shift while preserving a quite-sharp $B$ feature. Indeed, it has been noted by several authors that the intermediate spectra in this series (e.g., see the $x=0.5$ spectrum) are far too sharp to be a superposition of the end-point spectra, despite conventional discussions of the systems of magnetic properties in terms of dynamic Mn$^{3+}$/Mn$^{4+}$ mixtures.33 This quandary is underscored and compounded by noting that the structure of the $x=0.5$ main-edge spectrum changes only very slightly upon entering its low-temperature charge/orbital-ordered state.34

The Mn-K pre-edge feature spectral strength in this system has also been shown to track the Mn-valence/configuration change. The increase in the pre-edge feature strength, with increasing $x$, is illustrated in the inset of Fig. 6. The presence of three identifiable features $a1/a2/a3$ in the pre-edge of CaMnO$_3$ has been found to be characteristic of such Mn$^{4+}$ compounds.29 The crossover to a bimodal $a1/a2$ structure in $LaMnO_3$ is also clear in the Fig. 6 inset.

The main-edge spectra of the BCMO series shown in Fig. 7 sharply contrasts with these previous results (the differing crystal structure of the $x=0.0$ material motivates its separate consideration). While the $B$ feature of the BCMO series does shift systematically to lower energy with decreasing $x$, the $B$ feature also rapidly broadens and loses intensity to the region of the spectrum labeled $A$ in Fig. 7. Interestingly, plotting the
$B$-feature energy position versus $x$ for the (Bi, Ca) system (see Fig. 7 inset, lower right) reveals a quite good correlation with the (La, Ca) system despite the dramatically different edge-structural evolution in the two.

In Fig. 7, upper left, the pre-edge spectra of the BCMO series are shown. The spectral strength of these pre-edges decreases with decreasing $x$. This is consistent with the previous results on the LCMO system and with the decreasing Mn valence. The shift of intensity away from the $a2$ to the $a1$ portion of the spectrum is also consistent with that observed in the (La, Ca) system, with decreasing $x$ and decreasing Mn valence. The formation of a particularly sharp pre-edge feature in the BiMnO$_3$ is worth noting. In previous studies by our group on defected perovskites, the appearance of such features has correlated with the formation of noncentrosymmetric MnO$_6$ octahedra. Such local deviations from centrosymmetry would be consistent with the proposed “ferroelectric” distortions in BiMnO$_3$.

The crystal structure of BiMnO$_3$ is highly distorted. Indeed, it has been suggested that this material is in fact ferroelectrically/ferrodistortively distorted. The Mn-K main-edge spectrum for BiMnO$_3$ (see Fig. 7) displayed multiple unresolved features at the edge (see the labeled features 1–4 in Fig. 7). Ti-K edge studies of the ATiO$_3$ ($A =$ Ca, Sr, Ba, Pb) systems have shown that the multiplicity and splitting of the main-edge features increase with the increasing distortion in these ferrodistortive/ferroelectric perovskites. These main-edge splittings persist far above the ferroelectric transition temperatures in these Ti-based materials, leading authors to propose reinterpretation of the ferroelectricity as an order-disorder transition of the local distortions. The exceptionally large distortions in PbTiO$_3$ and BiMnO$_3$ have been attributed to the polarizability of the Pb/Bi 6$s^2$ states and their incorporation into covalent bonding with the O$_2$. The pronounced splitting of the Mn-K main-edge features is consistent with such local distortion effects.

It is tempting to associate the large modifications of the Mn main edge (upon Bi substitution into CaMnO$_3$) with disordered local distortions of the same sort that lead to the ferroelectricity in BiMnO$_3$. That such local distortions would persist at $x$ values far from the pure ferroelectric $x=0.0$ material is not unexpected in view of the local stability of distortions in the Ti compounds at temperatures far above the ferroelectric transition. To empirically test this notion, we have formed the difference spectra $\Delta \mu = [I(x)-xI(1.0)]/x$ for the BCMO series, where $I(x)$ is the Mn-K edge spectrum at a given $x$ (Fig. 8). This procedure “subtracts off” a fraction $x$ of sites assumed to remain CaMnO$_3$-like. While the authors believe that the CaMnO$_3$-like sites must in fact also evolve substantially with $x$, this method does provide a means of identifying subtle features in the $B$-feature broadening process.

Figure 8 displays the CaMnO$_3$ and BiMnO$_3$ spectra along with a series of $\Delta \mu$ difference spectra. As alluded to above, the subtraction procedure appears overzealous in the energy region of the CaMnO$_3$ $B$-feature peak (i.e. the “CaMnO$_3$-like” sites should not be $x$ independent). Nevertheless, there are strong structures in the $\Delta \mu$ spectra at energies close to the features labeled 2 and 4 in the BiMnO$_3$ spectrum. There is also a distinct shoulder at the feature-3 energy despite the fact that it rides on the oversubtracted $B$-feature dip. At the highest concentration ($x=0.4$) the buildup of intensity in the feature-1 region is also apparent. Thus our Mn-K main-edge XAS appears consistent with the notion that Bi substitution introduces locally distorted Mn sites into the BCMO system that are similar to those that lead to the ferroelectric distortion in BiMnO$_3$.

Work by Bridges et al. has shown modest but clear temperature dependences in the pre-edge spectra of the LCMO system in the ferromagnetic $0.2<x<0.5$ range. Recently, Qian et al. have confirmed this effect and also discovered a different thermal dependence accompanying the onset of robust charge/orbital ordering for $0.5<x<0.8$ in the LCMO system.

Figure 9 illustrates the variation of the Mn-K pre-edge features of the 0.6 material from above to below the charge/orbital-ordering temperature. As observed by Qian et al., the spectral intensity in the lowest-energy portion of the pre-edge (the $a1$-feature region) is reduced modestly in the CO phase. The same effect was seen in the $x=0.8$ system but with a much-smaller change, presumably due to the much-weaker charge ordering near the phase’s stability limit. The interpretation of these modest changes can be made here to...
motivate theoretical calculations. A small increase in the degree of Mn$^{4+}$ admixture accompanying the loss of ferromagnetic interactions upon entering the charge-ordered phase would at least be qualitatively consistent with the pre-edge feature change, i.e., the $a_1$ feature is weakened/shifted up with increasing Mn valence. A second possibility involves the orbital component at the increased Mn$^{3+}$ sites of the charge-ordered phase. Specifically, the static orbital alignment at these sites should be accompanied by a Jahn-Teller energy up-shift in the unoccupied $e_g$ states. Since the $a_1$ feature involves such $e_g$ states, the charge-ordered induced degradation of the low-energy side of the $a_1$ feature would be reasonable. Clearly the emergence of consistent pre-edge feature changes accompanying the phase changes in these materials should stimulate theoretical calculations of these spectral features.

**F. Mn-K EXAFS**

In order to compare the local structure unique of BCMO samples with LCMO samples, we have performed Mn-K-edge x-ray-absorption spectra measurements. Representative raw x-ray-absorption spectra data are shown in Fig. 10 as the inset for $x = 0.9$. Note that only small changes in amplitude occur with temperature.

In Fig. 10, we show the magnitude of the Fourier transform of the EXAFS$^* k^3$ spectra for selected materials in the BCMO system at 300 K. The first peak (~2 Å) corresponds to the Mn-O bond distribution. The second (~2.5 Å) and third peaks (~3.3 Å) contain the Mn-Ca/Bi and Mn-Mn correlations, respectively. The inset displays raw EXAFS$^* k^3$ data for $x = 0.9$ at 300 K (solid line) and 10 K (dotted line). Note that the temperature-dependent changes in amplitude are quite small.

and thermal disorder effects. Thus the Mn-O first shell in the Bi-substituted system appears to be disordered on a local scale relative to the LCMO system. The Bi-induced onset of charge/orbital-ordering correlations could contribute to this effect; however, work in our group has shown that the first Mn-O shell feature in the La$^{0.5}$Ca$^{0.5}$MnO$_3$ spectra do not show significant change upon entering the ordered state. The spectra above and below the charge-ordering temperature for the Bi$^{0.2}$Ca$^{0.8}$MnO$_3$ material also does not reveal an appreciable first-shell modification (Table I). Thus the local dis-

**FIG. 9.** Temperature-dependent pre-edge spectra of Bi$^{0.4}$Ca$^{0.6}$MnO$_3$. Note that the same trend occurs for $x = 0.4$ and 0.8.

**FIG. 10.** Magnitude of the Fourier transform of EXAFS$^* k^3$ $(2.5 \text{ Å}^{-1} \leq k \leq 12.3 \text{ Å}^{-1})$ for the system Bi$^{1-x}$Ca$_x$MnO$_3$ at 300 K. The first peak (~2 Å) corresponds to the Mn-O bond distribution. The second (~2.5 Å) and third peaks (~3.3 Å) contain the Mn-Ca/Bi and Mn-Mn correlations, respectively. The inset displays raw EXAFS$^* k^3$ data for $x = 0.9$ at 300 K (solid line) and 10 K (dotted line). Note that the temperature-dependent changes in amplitude are quite small.

**FIG. 11.** Magnitude of the Fourier transform of EXAFS$^* k^3$ $(2.5 \text{ Å}^{-1} \leq k \leq 12.3 \text{ Å}^{-1})$ for the system La$^{1-x}$Ca$_x$MnO$_3$ at 300 K. The first peak (~2 Å) corresponds to the Mn-O bond distribution. The second (~2.5 Å) and third peaks (~3.3 Å) contain the Mn-Ca/La and Mn-Mn correlations, respectively.
tortions in the Mn-O shell in the BCO system appear to be related to the local effect of the Bi substitution and not to the longer-range charge/orbital-ordering distortions. In fact, in systematic temperature-dependent x-ray-absorption spectra measurements of the 0.8 and 0.9 systems, no significant changes in the Mn-O peak shape occur with temperature.

Detailed first-shell fits were performed on x = 0.8 and 0.9 as well as on the x = 1.0 and these results are reported in Table I. For high-Bi content (x > 0.8) the spectra can not be modeled by Gaussian distributions or cumulants (expansion does not converge) because of the high level of local structural distortions. This is consistent with the very large distribution of Mn-O distances found by neutron diffraction in the x = 0 end member BiMnO₃.¹⁸

Referring again to the BCO results in Fig. 10, the higher-shell Mn-Bi/Ca and Mn-Mn coordination peaks are seen to be systematically reduced in amplitude with increased Bi content and in Fig. 11 they were compared to the LCMO system. This implies that the higher Bi-concentration samples are increasingly disordered. Again the potential role of charge/orbital ordering in this disordering effect must be considered. Work in our group has shown that the third-shell (Mn-Mn) feature is strongly reduced in the ordered (low-temperature) phase of the La₀.₅Ca₀.₅MnO₃ material. Thus the increasing higher-shell disorder (with increasing Bi content) in the BCO system would appear to involve a charge/orbital-ordering contribution in addition to the local Bi-distortion contribution. Hence, local disorder induced by the Bi-6s² lone pairs stabilize charge ordering over a large-doping (x) range and suppresses the e₉ hopping mediated metallic state.

V. CONCLUSION

Systematic structural, magnetic, and transport studies on the BCO system were reported for the doping range x ≥ 0.4. These measurements were correlated with x-ray absorption spectroscopy measurements. The XAS measurements clearly indicate that increasing Bi content in CaMnO₃ stabilizes increasing Mn³⁺ character similar to the LCMO system. However, the XAS results also indicate that very substantial local distortions about the Mn sites accompany the Bi substitution in contrast to the LCMO system. Indeed, the x-ray diffraction data reveal splittings consistent with lower-symmetry cells as Bi content increases.

The phase diagram of the BCO system (and the magnetic and transport properties on which it is based) resembles the LCMO system in some aspects, and differs in others. The similarities to be noted are as follows. At room temperature FM interactions and enhanced electrical conductivity (decreased resistivity) are rapidly stabilized by small levels of A³⁺ substitution. FM fluctuations dominate the
high-temperature region for \( x \approx 0.95 \). A robust FM component is incorporated into the AF ground state with the maximum of this FM component correlating with the maximum conductivity enhancement near \( x = 0.875 \). A charge/orbital-plus AF-ordered phase onset near \( x = 0.83 \), below which a line of CO ordering transition temperatures \( T_{CO} \) rises steeply, with decreasing \( x \) in the phase diagrams.

A strong disparity with the LCMO system lies in the substantially more robust character of the charge-ordered state in the LCMO system. This remains high for extending down to 0.4 as opposed to \( T_{CO} \) declining and the ground state converting to an FM metal below \( x = 0.5 \) in the LCMO system. Presumably the local Mn-O distortions stabilize the local charge/orbital-ordering process.

In general the FM-metal-to CO-ordered insulator transition manifests the most precipitous field-sensitive conductivity change in manganite materials. Bi substitution appears to most efficiently stabilize the CO-ordering to above room temperature. Thus the use of Bi admixture in materials with high-temperature FM-metal transition temperatures may be an avenue to bring these two phenomena into competition in the room-temperature range.

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