Synthesis and characterization of Ca-doped LaMnAsO

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Abstract
We report on our attempt to hole-dope the antiferromagnetic semiconductor LaMnAsO by substitution of the La3+ site by Ca2+. We use neutron and x-ray diffraction, magnetic susceptibility, and transport techniques to characterize polycrystalline (La1−xCax)MnAsO samples prepared by solid-state reaction and find that the parent compound is highly resistant to substitution with an upper limit x≤0.01. Magnetic susceptibility of the parent and the x=0.002 (xnom=0.04) compounds indicate a negligible presence of magnetic impurities (i.e., MnO or MnAs). Rietveld analysis of neutron and x-ray diffraction data shows the preservation of both the tetragonal (P4/nmm) structure upon doping and the antiferromagnetic ordering temperature, TN=355±5 K.

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Synthesis and characterization of Ca-doped LaMnAsO
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We report on our attempt to hole-dope the antiferromagnetic semiconductor LaMnAsO by substitution of the La\(^{3+}\) site by Ca\(^{2+}\). We use neutron and x-ray diffraction, magnetic susceptibility, and transport techniques to characterize polycrystalline (La\(_{1-x}\)Ca\(_x\))MnAsO samples prepared by solid-state reaction and find that the parent compound is highly resistant to substitution with an upper limit \(x \lesssim 0.01\). Magnetic susceptibility of the parent and the \(x = 0.002\) (\(x_{\text{nom}} = 0.04\)) compounds indicate a negligible presence of magnetic impurities (i.e., MnO or MnAs). Rietveld analysis of neutron and x-ray diffraction data shows the preservation of both the tetragonal (\(P4/nmm\)) structure upon doping and the antiferromagnetic ordering temperature, \(T_N = 355 \pm 5\) K.

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I. INTRODUCTION

Recent studies on hole-doped BaMn\(_2\)As\(_2\) by substitution of the Ba site with K [i.e., (Ba\(_{1-x}\)K\(_x\))M\(_2\)As\(_2\)] reveal a remarkable coexistence of local-moment antiferromagnetism (AFM) associated with the Mn site and itinerant weak ferromagnetism (FM) associated with the As electronic bands [1]. Studies of the extended parent BaMn\(_2\)P\(_2\) (\(Pn = P, As, and Sb\); referred to as Mn-122) compounds indicate appreciable spin-dependent Mn-Pn hybridization that induces relatively strong Mn-Mn superexchange coupling leading to a \(G\)-type checkerboard ground state in the undoped parent compounds [2]. The unique Mn-Pn hybridization in BaMn\(_2\)P\(_2\) is different than that in the isostructural Ba\(_2\)T\(_2\)P\(_2\) (\(T = Fe, Co, and Ni\)) compounds [2], which may explain why doping BaFe\(_2\)As\(_2\) with Mn does not induce superconductivity but rather shows a local-moment behavior [2].

The appearance of itinerant FM by hole doping of BaMn\(_2\)As\(_2\) prompted us to search for other related systems that possess the MnAs layers, such as LnMnAsO, (\(Ln = La, Ce, P, and Nd\); referred to as Mn-1111 compounds), that can potentially extend the universality of the AFM-FM coexistence phenomena. LnMnPnO are layered compounds with a MnAs layer as in BaMn\(_2\)P\(_2\) that are separated by an LnO layer. Various studies of the parent LnMnPnO have shown that the MnPn planes are universally antiferromagnetic [3–10] with in-plane checkerboard magnetic structure similar to the in-plane magnetic ordering in the various Mn-122 compounds. For compounds with moment-bearing rare-earth ions (\(Ln\), a second low temperature magnetic ordering of the rare-earth element (i.e., Ce, Nd, and Pr) accompanied by a Mn-spin reorientation transition have been observed [4–9]. Other Mn-1111 compounds with variations on the \(Ln\) or \(Pn\) sites have also been shown to order with the same in-plane AFM structure, albeit with uniform or alternate stacking of the AFM planes [11,12].

Doping the Mn-1111 compounds by substitution of the \(Ln\) site has proven difficult and with the extra complication of the inevitable presence of magnetic impurity phases (i.e., MnO and MnAs) that obfuscate the nature of the magnetism in the compound of interest. In particular, it has been proven difficult to avoid the presence of small amounts of MnAs that is FM below around 310 K with a complicated magnetic field dependent magnetostuctural transition temperature [13]. Indeed, it has been reported that Sr substitution of the AFM (La\(_{1-x}\)Sr\(_x\))MnAsO is limited to doping levels below \(x \approx 0.1\) with a robust resistance “against carrier doping” [14]. However, even minute doping of Sr for La leads to a significant reduction in resistivity at room temperature, and the doped samples display measurable thermoelectric properties [14]. Magnetic susceptibility measurements of the Sr substituted samples exhibit weak anomalies around room temperature that may arise from a MnAs impurity phase [14]. Another approach to doping the LaMnAsO system is by substituting the oxygen site with hydrogen by solid-state reaction at high pressure to yield LaMnAsO\(_{1-x}\)H\(_x\) with \(0 < x < 0.7\) [15]. The hydrogen doping suppresses AFM for \(x \geq 0.1\) and as \(x\) is increased, FM sets in with a \(T_c\) that increases gradually with \(x\), with no evidence of AFM-FM coexistence [15].

Here, we report on our effort to dope LaMnAsO with hole carriers by substituting the La\(^{3+}\) site by Ca\(^{2+}\) by using various experimental techniques. LaMnAsO orders in AFM structure at \(T_N = 360\) K [4] above which short-range magnetic order with strong two-dimensional-like characteristics has been observed up to \(T \sim 650\) K [10]. Inelastic neutron scattering from LaMnAsO shows rodlike spin waves spectra that extend beyond 30 meV with a 3.5-meV gap below \(T_N\) indicating very weak interlayer coupling. It has also been suggested that chemical substitution or pressure may switch the sign of the interlayer exchange coupling [10].
II. EXPERIMENTAL DETAILS

Polycrystalline samples of (La$_{1-x}$Ca$_x$)MnAsO are synthesized via a two-step solid-state reaction. The chemicals are weighed and ground in a glovebox under argon atmosphere. La filings, Ca pieces, and As powder are initially fired at 500 °C in a La:Ca:As = 1 − x : x : 1 (0 ≤ x ≤ 0.12) molar ratio. We note that x is the nominal or target composition and not the actual value as discussed below. A stoichiometric amount of MnO powder is then mixed with the prereacted (La$_{1-x}$Ca$_x$)As, and finely ground into a mixture that is pressed into pellets under pressure of 12 MPa, and sintered at 1100 °C for 12 h in an evacuated quartz tube. The chemical composition of the samples is examined by energy dispersive x-ray spectroscopy (EDS) that shows the nominally prepared samples with x$_{\text{nom}}$ = 0, 0.04, 0.08, and 0.12 are deficient of Ca with x$_{\text{EDS}}$ = 0.0, 0.002, 0.006, and 0.008, respectively. (From here on, x refers to the EDS value.)

Powder x-ray diffraction measurements are performed on a PANalytical MPD diffractometer using Co Kα radiation. X-ray diffraction patterns for x = 0, 0.002, 0.006, and 0.008, are shown in Fig. 1 indicating an increase of various impurities as x increases. Powder diffraction analysis using the FULLPROF program [16] shows that neither MnO nor MnAs is not detectable in the parent compound (x = 0), however, both impurities are clearly present for the x = 0.002 compound. To account for other extra peaks in the diffraction patterns, we have tried to include other compounds as impurities, for instance, CaO, LaOH, As, As$_2$O$_3$, Ca, Ca(OH)$_2$, CaLa$_3$[SiO$_4$]$_2$[AsO$_4$]O, CaAs, CaCO$_3$(calc), CaCO$_3$(vat), CaMn$_2$As$_2$, La, La$_2$O$_3$, LaAs, LaH$_2$, Mn, and SiO$_2$ which do not peak in the x-ray sets.

FIG. 1. Powder x-ray diffraction patterns for nominally Ca-La substituted samples (La$_{1-x}$Ca$_x$)MnAsO as indicated. The patterns are shifted for clarity, and x$_{\text{nom}}$ refers to the nominal amount in the preparation, and x$_{\text{EDS}}$ is the amount determined by EDS (from here on for consistency we use EDS value). The curves below the data show the difference between the best fit and the data. The tick marks at the bottom of the figure show the expected peaks of pure LaMnAsO. The dashed vertical lines show the peak positions of prominent diffraction peaks of MnO and MnAs as indicated.

FIG. 2. Field-cooled magnetic susceptibility, $\chi = M/H$, of a (La$_{1-x}$Ca$_x$)MnAsO polycrystalline sample measured in the temperature range of 10–700 K, at a magnetic field of H = 1.0 T. $T_N$ is the Néel temperature determined from the neutron diffraction data. The dashed line labeled $T_C$-MnAs indicates the Curie temperature of MnAs [13], and the $T_N$-MnO is the Néel temperature of MnO.

FIG. 3. Resistivity as a function of temperature from pellets of (La$_{1-x}$Ca$_x$)MnAsO for x = 0 and x = 0.002 (x$_{\text{nom}}$ = 0.04), as indicated. The solid lines are fit to Eq. (1).
THE vertical bars are the expected Bragg peak positions as mentioned in the panels. Additional peaks from Al and austenitic steel (sample holder and furnace) are also included. Possible positions for MnO impurity peaks are also shown.

Resistivity and magnetization measurements are performed by using a physical property measurement system (Quantum Design) equipped with a vibrating sample magnetometer. Figure 2 shows magnetic susceptibility measurements of the parent and the doped samples. As for other Mn-1111 samples, the susceptibility does not exhibit a clear anomaly at or around $T_N$ consistent with previous reports [9,10,12]. The doped samples show anomalies around room temperature that indicate the presence of MnAs ($T_N \approx 310$ K). Assuming the saturated moment per Mn in MnAs is $3.4 \mu_B$ [17], we estimate the present MnAs at levels of few micrograms per gram of sample, generally negligible to yield a signal in x-ray diffraction. We therefore caution that the susceptibility reported in Ref. [3] showing a FM signal around $T = 310$ K in LaMnAsO is likely due to MnAs impurities in that sample.

Neutron powder diffraction (NPD) measurements on polycrystalline samples are performed on the high-resolution powder diffractometer at the University of Missouri Research Reactor using a double-focusing Si(511) crystal monochromator to select neutrons with a wavelength $\lambda = 1.486$ Å. For the NPD measurements, 2 g of polycrystalline LaMnAsO was loaded into a vanadium cell that was subsequently held inside of an aluminum exchange gas can; and 4 g nominal (La$_{1-x}$Ca$_x$)MnAsO ($x = 0.04$) was loaded into an aluminum sample holder that was similarly held in a helium exchange gas. The aluminum can was later chosen in order to minimize the background in light of the broad two-dimensional (2D) magnetic scattering. A set of five linear position-sensitive detectors are employed to collect a series of $2\theta = 19^\circ$ sections of the diffraction pattern; the full diffraction pattern is measured in five steps to a $2\theta_{\text{max}} = 108^\circ$. This powder diffractometer uses a radial oscillating collimator that averages the shadow of the collimator blades at every channel. The large detector areas allow very weak magnetic peaks to be detected by neutrons with high statistical accuracy. The NPD is collected using a high-temperature furnace. Analysis of the NPD data is performed by the Rietveld method using the FULLPROF program [16].

III. RESULTS AND DISCUSSION

Our x-ray diffraction, susceptibility measurements, and elemental analysis all indicate that LaMnAsO is highly resistant to Ca doping with increased interfering impurities with the increase of nominal Ca concentration. However, transport

FIG. 4. Observed neutron diffraction patterns (red open circles) for (La$_{1-x}$Ca$_x$)MnAsO, fits from the Rietveld refinement (black solid lines), and their differences (dark-yellow solid lines) at (a) $T = 400$ K ($>T_N$) and (b) $T = 300$ K ($<T_N$) for (I) $x = 0.0$ and (II) $x = 0.002$. The vertical bars are the expected Bragg peak positions as mentioned in the panels. Additional peaks from Al and austenitic steel (sample holder and furnace) are also included. Possible positions for MnO impurity peaks are also shown.

FIG. 5. Illustration of chemical and magnetic structure of LaMnAsO.
Type parameters and the unit cell volume, respectively. Combined magnetic/nuclear Bragg peaks below and slightly above the parent 002 samples (formed into pellets and polished) compared to the parent x = 0 one. Fitting the resistivity as a function of temperature to a standard semiconductor resistivity of the form

$$\rho = AT^{-3/2}e^{-E_g/k_B T},$$

we find that the semiconducting gap $E_g = 0.21$ eV for LaMnAsO ($x = 0.0$) and a more complicated behavior for the $x = 0.002$ sample with an effective gap $E_g' \sim 0.03$ eV. Such a dramatic change upon hole doping by Sr has been reported for (La$_{1-x}$Sr$_x$)MnAsO [14]. At this level of doping we presume that the decrease in resistivity is likely due to formation of a hole level by acceptor doping with an effective narrower energy gap.

Panels I and II in Figure 4 show the full powder neutron diffraction patterns obtained at $T = 400$ K ($>T_N$) and $T = 300$ K ($<T_N$), as indicated for the two samples. The diffraction patterns at both temperatures include diffraction peaks from the aluminum and austenitic steel sample holder and/or exchange gas can in the furnace. In addition, we observe minute impurities in the two samples that could not be identified as MnAs, or various potential compounds that could be formed with the ingredients of these samples (listed in the Experimental Details). Rietveld structural refinement of the nuclear structure at high temperature is performed using the tetragonal $P4/nmm$ crystal symmetry. For the doped compound, the inclusion of MnO (in minute amounts) improves the refinement slightly but MnAs does not, in agreement with our x-ray refinement analysis.

The magnetic structure is determined from the combined nuclear and magnetic Rietveld refinement of the diffraction pattern at $T = 300$ K, yielding a C-type AFM ordering with the

TABLE I. Fit parameters obtained from Rietveld refinements of the powder neutron diffraction patterns at the two listed temperatures with tetragonal $P4/nmm$ space group with La at ($\frac{1}{4}, \frac{1}{4}, z_{La}$), Mn at ($\frac{1}{4}, \frac{1}{4}, \frac{1}{2}$), As at ($\frac{1}{2}, \frac{1}{2}, 0$), and O at ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$), and $a$, $c$, and $V$ are the unit cell parameters and the unit cell volume, respectively. $d_{\text{Mn-As}}$ are the in-plane Mn-As distances, respectively. $\mu$ is the extracted average magnetic moment at $T = 300$ K. The error (one standard deviation) in the last digit of a quantity is shown in parentheses.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$x$</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$c/a$</th>
<th>$V$ ($\text{Å}^3$)</th>
<th>$z_{\text{As}}$</th>
<th>$d_{\text{Mn-As}}$ (Å)</th>
<th>$\mu$ (μA)</th>
</tr>
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<tbody>
<tr>
<td>Neutron 300</td>
<td>0.0</td>
<td>4.130(2)</td>
<td>9.0501(5)</td>
<td>2.196(1)</td>
<td>152(1)</td>
<td>0.1330(5)</td>
<td>0.6693(5)</td>
<td>2.528(7)</td>
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<tr>
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<td>9.082(1)</td>
<td>2.1970(3)</td>
<td>155.2(2)</td>
<td>0.139(4)</td>
<td>0.6697(4)</td>
<td>2.578(7)</td>
<td>2.3(1)</td>
</tr>
<tr>
<td>400</td>
<td>0.0</td>
<td>4.1337(3)</td>
<td>9.082(1)</td>
<td>2.1971(3)</td>
<td>155.2(2)</td>
<td>0.1331(7)</td>
<td>0.6688(7)</td>
<td>2.563(7)</td>
</tr>
<tr>
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<td>9.0594(7)</td>
<td>2.1963(2)</td>
<td>154.1(2)</td>
<td>0.1330(4)</td>
<td>0.6696(4)</td>
<td>2.572(7)</td>
<td></td>
</tr>
</tbody>
</table>

FIG. 6. Intensity versus 2$\theta$ around the (100) magnetic and (101) combined magnetic/nuclear Bragg peaks below and slightly above $T_N$ for (La$_{1-x}$Ca$_x$)MnAsO at (a) $x = 0.0$ and (b) $x = 0.002$.

FIG. 7. Integrated intensity ($I_M$) of the (1 0 1) Bragg peak as a function of temperature $T$ for (La$_{1-x}$Ca$_x$)MnAsO at (a) $x = 0.0$ and (b) $x = 0.002$. The solid line is a power-law fit given by $I_M \propto I_0(1 - T/T_N)^{\beta}$, for $300 \leq T \leq 355$ K. The rest of the data for $T > 355$ K is fitted using a linear term.
magnetic Mn$^{2+}$ moments aligned along the c axis and arranged antiferromagnetically in the tetragonal basal plane and stacked ferromagnetically along the c axis, as shown in Fig. 5. The value of the ordered moment at $T = 300 \, \text{K}$ is found to be $\mu = 2.3(1) \, \mu_{\text{B}}/\mu_{\text{Mn}}$ for the parent and the $x = 0.002$ samples, respectively. These values agree with those obtained previously for LaMnAsO [4,10] or CeMnAsO [9] at $T = 300 \, \text{K}$. The fit parameters from the Rietveld refinements of the diffraction patterns are listed in Table I showing negligible differences between the $x = 0$ and the $x = 0.002$ samples.

For the temperature dependence of the magnetic order parameter we use the integrated intensity of the magnetic (100) and the nuclear/magnetic (101) peaks (in the $19^\circ \leq \theta \leq 26^\circ$ region) as shown in Fig. 6. As the temperature is raised above $T_N \sim 360 \, \text{K}$, broad magnetic scattering intensity is found to persist up to the highest temperature we measured (i.e., $T = 400 \, \text{K}$) where the two peaks merge into an asymmetric peak characteristic of a diffraction pattern from a 2D polycrystalline system with so-called Warren line shape [18]. Such 2D diffraction above $T_N$ is consistent with previous observations in other Mn-1111 compounds [9,10,12]; however, the shape of the merged peaks above $T_N$ in Ref. [10] seems to be symmetric.

The temperature dependence of the integrated intensities of both the (100) and the (101) peaks for both samples (normalized to 1 g sample) are shown in Fig. 7. We fit the integrated intensity to a power law with a critical exponent $\beta$, given by $I_\text{M} \propto I_0 (1 - T/T_N)^{\beta}$, which yields $T_N = 355 \pm 5 \, \text{K}$ and $\beta \approx 0.366$. The fact that $T_N$ is the same within error for both samples is not proof that substitution of Ca on the La site does not occur. It has been shown that $T_N$ in the MnAs layer of Mn-122 compounds is robust against substitution of the layers adjacent to it. Indeed, substituting K for Ba in Ba$_{1-x}$K$_x$Mn$_2$As$_2$ shows that $T_N$ of the MnAs layers changes negligibly in the range $0 \leq x \leq 0.2$ [19,20]. Figure 8 shows the linewidths of the (100) and (101) as a function of temperature that are extracted from fitting the diffraction patterns in scans similar to those in Fig. 6 using two Gaussian peaks indicating finite 2D magnetic correlations at $T \sim 400 \, \text{K}$ with a rough estimate of $\sim 30 \, \text{Å}$ in length scale.

IV. CONCLUSION

Our attempt to hole-dope the antiferromagnetic LaMnAsO is met with a robust resistance to substitution of the La site by Ca in (La$_{1-x}$Ca$_x$)MnAsO to a limited $x = 0.008$ ($x_{\text{nom}} = 0.12$) and likely even lower. Our solid-state reaction method produces a high-quality parent sample that is free of the commonly observed MnAs and MnO impurities. Nevertheless, resistivity measurements show that the parent compound has a relatively small semiconducting gap $E_g \approx 0.2 \, \text{eV}$ and doping with a minute amount of Ca $x = 0.002$ ($x_{\text{nom}} = 0.04$) lowers the resistivity by approximately three orders of magnitude. Our neutron powder diffraction of the $x = 0$ and the nominal $x = 0.002$ samples is consistent with known behaviors of the general Mn-1111 samples where the Mn subsystem is AFM with moments aligned along the c axis and that above $T_N$, 2D short-range AFM ordering persists to much higher temperatures that is close to the transition temperature of the Mn-122 systems for which $T_N \sim 600 \, \text{K}$.

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