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Phys. Rev. B **84**, 014405 — Published 20 July 2011

DOI: [10.1103/PhysRevB.84.014405](https://doi.org/10.1103/PhysRevB.84.014405)

Observation of a Large Miscibility Gap in the $\text{Ba}(\text{Mn}_x\text{Fe}_{1-x})_2\text{As}_2$ System

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The compounds BaMn_2As_2 and BaFe_2As_2 both crystallize in the body-centered-tetragonal ThCr_2Si_2 -type (122-type) structure at room temperature but exhibit quite different unit cell volumes and very different magnetic and electronic transport properties. Evidently reflecting these disparities, we have discovered a large miscibility gap in the system $\text{Ba}(\text{Mn}_x\text{Fe}_{1-x})_2\text{As}_2$. Rietveld refinements of powder x-ray diffraction (XRD) measurements on samples slow-cooled from 1000°C to room temperature (RT) reveal a two-phase mixture of BaMn_2As_2 and $\text{Ba}(\text{Mn}_{0.12}\text{Fe}_{0.88})_2\text{As}_2$ phases together with impurity phases for $x = 0.2, 0.4, 0.5, 0.6$ and 0.8 . We infer that there exists a miscibility gap in this system at 300 K with composition limits $0.12 \lesssim x \lesssim 1$. For samples quenched from 1000°C to 77 K , the refinements of RT XRD data indicate that the miscibility gap at RT narrows at 1000°C to $0.2 \lesssim x \lesssim 0.8$. Samples with $x = 0.4, 0.5$ and 0.6 quenched from 1100 – 1400°C to 77 K contain a single 122-type phase together with significant amounts of $\text{Fe}_{1-x}\text{Mn}_x\text{As}$ and FeAs_2 impurity phases. These results indicate that the system is not a pseudo-binary system over the whole composition range and that the 122-type phase has a significant homogeneity range at these temperatures. Magnetic susceptibility χ , electrical resistivity ρ and heat capacity measurements versus temperature T of the single-phase quenched polycrystalline samples with $x = 0.2$ and 0.8 are reported. We also report attempts to grow single crystals of the substituted compounds $\text{Ba}(\text{Mn}_{1-x}\text{T}_x)_2\text{As}_2$ ($T = \text{Cr, Fe, Co, Ni, Cu, Ru, Rh, Pd, Re, Pt}$) and $\text{BaMn}_2(\text{As}_{1-x}\text{Sb}_x)_2$ out of Sn flux. Energy dispersive x-ray analyses show that most of these elements do not substitute into the lattice in amounts greater than 0.5% . However, concentrations of 4.4% , $\sim 10\%$ and 2.6% were achieved for Cr, Fe and Sb substitutions, respectively, and $\chi(T)$ and $\rho(T)$ data for these crystals are presented.

PACS numbers: 74.70.Xa, 64.75.Nx, 75.40.Cx, 75.50.Ee

I. INTRODUCTION

The discovery¹ of superconductivity at 26 K in $\text{LaFeAsO}_{1-x}\text{F}_x$ with the tetragonal ZrCuSiAs -type structure in 2008 motivated many efforts to understand the superconducting pairing mechanism and to discover additional families of Fe-based superconductors.² New parent compounds $A\text{Fe}_2\text{As}_2$ ($A = \text{Ba, Sr and Ca}$) that crystallize in the related tetragonal ThCr_2Si_2 -type (122-type) structure, together with other families, were soon discovered.² Among 122-type materials, BaFe_2As_2 has gained much attention as a parent compound because superconductivity can be induced in this material by various means, *i.e.*, by applying pressure^{3–5} and by substitutions at the Ba site (by K)⁶, at the Fe site (by Co, Ni, Ru, Rh, Pd)^{2,7} and at the As site (by P).⁸ An interesting result is that while electron doping by Co, Ni, Rh and Pd at the Fe site in BaFe_2As_2 induces superconductivity, hole doping by Cr and Mn for Fe does not.^{9–12}

The reported experimental results and electronic structure calculations demonstrate that the physical properties of BaCr_2As_2 and BaMn_2As_2 are significantly different from those of BaFe_2As_2 .^{13–16} In particular, the unit cell volume of BaMn_2As_2 (234.12 \AA^3) is much larger than that of BaFe_2As_2 (204.38 \AA^3),² in spite of the fact that Mn and Fe are $3d$ transition-metal neighbors in the periodic table. This divergence suggests that the Mn^{+2} is in a high-spin state while, in a local moment model, Fe^{+2} is in a low-spin state. BaMn_2As_2 is an antiferromagnetic insulator with a large ordered moment of $3.9\mu_{\text{B}}/\text{Mn}$ and a high Néel temperature $T_{\text{N}} = 625\text{ K}$ (Ref. 16) whereas BaFe_2As_2 is an itinerant antiferromagnet with a much lower ordered moment of $0.9\mu_{\text{B}}/\text{Fe}$ and a much lower $T_{\text{N}} = 137\text{ K}$.² In addition, the antiferromagnetic structure of BaMn_2As_2 is Néel-type (G-type or checkerboard-type) with the ordered moments aligned along the tetragonal c axis,¹⁶ whereas that of BaFe_2As_2 is a type of antiferromagnetic stripe structure with the ordered moments aligned in the ab plane.²

There have been a number of investigations of iron-arsenide compounds in which the Fe is partially substituted by Mn.^{10,12,17–22} For $A\text{Fe}_2\text{As}_2$ -type materials, a maximum of 17.6% and 18% Fe substitution by Mn was reported for BaFe_2As_2 (Ref. 12) and SrFe_2As_2 (Ref. 18), respectively. Although the Mn doping leads to suppression of the magnetic/structural transition to lower temperatures, the reported results suggest that doping with Mn is detrimental to the occurrence of superconductivity and in most cases it leads to a magnetic and more resistive ground state.^{10,12,17–21} It has been reported that in hole-doped systems, besides the changes in the electronic structure introduced by the dopant, the resultant variation of the Fe-As bond length plays a crucial role in defining nature of the ground state.^{18,20} The variation of Fe-As bond length for K- and Mn-doped SrFe_2As_2 is significantly different.¹⁸ In none of these studies of $A(\text{Mn}_x\text{Fe}_{1-x})_2\text{As}_2$ systems was the possible existence of a miscibility gap in the phase diagram mentioned.

The peculiar properties of BaMn_2As_2 suggest that this compound may be a bridge between the BaFe_2As_2 -type

materials and the more ionic high- T_c cuprates.^{15,16} This in turn suggests that if BaMn_2As_2 could be doped into the metallic state, the resulting compounds might have interesting superconducting properties. This possibility motivated our attempts to grow single crystals of substituted BaMn_2As_2 , as will be discussed. However, we found that the attempted substitutions usually failed to achieve concentrations above 0.5%. In the case of Fe substitutions for Mn, the single crystals contained a maximum of $\sim 10\%$ Fe substituted for Mn. It was not clear to us whether such limits arose from peculiarities of the crystal growths, or were intrinsic to the equilibrium phase diagrams. To investigate this question, we chose to study $\text{Ba}(\text{Mn}_x\text{Fe}_{1-x})_2\text{As}_2$ in more detail as a prototype system using polycrystalline samples. We discovered a wide miscibility gap in this system in slow-cooled samples, that only narrows slightly for samples quenched from 1000 °C to 77 K. Magnetic susceptibility χ , electrical resistivity ρ and heat capacity C_p versus temperature T data for single-phase polycrystalline $\text{Ba}(\text{Mn}_{0.2}\text{Fe}_{0.8})_2\text{As}_2$ and $\text{Ba}(\text{Mn}_{0.8}\text{Fe}_{0.2})_2\text{As}_2$ samples quenched from 1000 °C will be reported. We also present $\rho(T)$ and/or $\chi(T)$ data for several of the above-mentioned lightly-doped crystals.

The remainder of the paper is organized as follows. The experimental details are given in Sec. II. The phase analyses and structures of polycrystalline and single crystal samples with nominal composition $\text{Ba}(\text{Mn}_x\text{Fe}_{1-x})_2\text{As}_2$, which establish the miscibility gap, are given in Sec. III. The physical properties of the single-phase polycrystalline $\text{Ba}(\text{Mn}_{0.2}\text{Fe}_{0.8})_2\text{As}_2$ and $\text{Ba}(\text{Mn}_{0.8}\text{Fe}_{0.2})_2\text{As}_2$ samples quenched from 1000 °C are presented in Sec IV. Our $\chi(T)$ and $\rho(T)$ data for substituted single crystals of BaMn_2As_2 are presented in Sec. V. A summary of this work and our conclusions are given in Sec. VI.

II. EXPERIMENTAL DETAILS

Polycrystalline samples of $\text{Ba}(\text{Mn}_x\text{Fe}_{1-x})_2\text{As}_2$ ($x = 0.2, 0.4, 0.5, 0.6$ and 0.8) were synthesized by solid state reaction using Ba (99.99%) from Sigma-Aldrich, and Fe (99.998%), Mn (99.95%) and As (99.99999%) from Alfa-Aesar. Stoichiometric mixtures of the elements were pelletized and placed in alumina crucibles that were sealed inside evacuated silica tubes. The samples were heated to 585 °C at a rate of 40 °C/h, held there for 20 h, then heated to 620 °C at a rate of 7 °C/h, held there for 20 h, and finally heated to 750 °C at 30 °C/h and held there for 25 h. The samples were then thoroughly ground, pelletized and again sealed in evacuated silica tubes. The samples were fired at 750 °C and then at 1000 °C for 20 h and 80 h, respectively, followed by furnace-cooling (“slow-cooling”). For quenching experiments, pressed pellets were wrapped in Ta foil and sealed in silica tubes containing $\sim 1/3$ atm of Ar. The tubes were then heated to temperatures ranging from 1000 to 1400 °C for 2–20 h and then quenched into liquid nitrogen at 77 K. There was no evidence that the samples reacted with either the Ta foils or the silica tubes during these quenching experiments.

Structural characterization of the polycrystalline samples was performed using powder x-ray diffraction (XRD) data obtained from a Rigaku Geigerflex powder diffractometer and CuK_α radiation. The FullProf package was used for Rietveld refinement of the XRD data.²³

Attempts to grow single crystals of $\text{Ba}(\text{Mn}_{1-x}\text{T}_x)_2\text{As}_2$ ($T = \text{Cr, Fe, Co, Ni, Cu, Ru, Rh, Pd, Re}$ and Pt) and $\text{BaMn}_2(\text{As}_{1-x}\text{Sb}_x)_2$ were made using Sn flux. To begin, polycrystalline samples of $\text{Ba}(\text{Mn}_{1-x}\text{T}_x)_2\text{As}_2$ or $\text{BaMn}_2(\text{As}_{1-x}\text{Sb}_x)_2$ were synthesized using the method described above and then ~ 200 mg of a sample was placed in an alumina crucible together with Sn, using a sample to Sn molar ratio of 1 : 45. The top of the crucible was packed with quartz wool. The alumina crucible was sealed inside a silica tube under a pressure of $\sim 1/3$ atm Ar. The sample was heated to 1100 °C at a rate of 40 °C/h, held there for 40 h, and then cooled to either 700 °C or 900 °C at a rate of 4 °C/h. At the respective temperature the Sn flux was decanted using a centrifuge. The typical size of the shiny plate-like crystals obtained was $2 \times 2 \times 0.2$ mm³.

The chemical compositions of the crystals grown in Sn flux were measured by energy dispersive x-ray (EDX) analysis using a JEOL scanning electron microscope. The EDX results showed that most growth attempts resulted in substitutions of less than 0.5% except for the cases of Cr, Fe and Sb where 4.4%, $\sim 10\%$ and 2.6% substitutions were obtained, respectively, as shown in Table I. A more detailed study of the compositions of Fe-substituted crystals is given in Sec. III C.

An interesting result is that in contrast to the case of BaFe_2As_2 crystals grown in Sn flux where up to 2–3 at% of Sn with respect to Fe becomes incorporated into the crystals²⁴ that drastically modifies their physical properties,^{25–27} Sn enters the crystal lattice of pure or lightly substituted BaMn_2As_2 in much smaller amounts (see Table I). Consistent with this result, our lightly Cr-, Fe- and Sb-substituted crystals were found to have magnetic properties very similar to those of pure BaMn_2As_2 , as will be shown in Sec. V.

Field- and temperature-dependent magnetization measurements were carried out using a superconducting quantum interference device magnetometer (Quantum Design, Inc.). Heat capacity measurements were done using a thermal relaxation technique with a Quantum Design physical property measurement system (PPMS).

Electrical resistivity measurements were carried out using a four-probe ac method in the PPMS. Contacts of the

TABLE I: Measured values of the content of transition metals ($T = \text{Cr, Fe, Co, Ni, Cu, Ru, Rh, Pd, Re}$ and Pt) and Sb present in the Sn-grown Mn- and As-rich crystals of $\text{Ba}(\text{Mn}_{1-x}\text{T}_x)_2\text{As}_2$ and $\text{BaMn}_2(\text{As}_{1-x}\text{Sb}_x)_2$, respectively. A value of “0” means that the EDX measurement software gave this value with no error bars. The Sn content is the atomic fraction with respect to the total transition metal content. The Fe-substituted sample with high Fe concentration marked by an asterisk is Crystal-1 in Table III below, for which the Fe and Sn concentrations at two different points on the crystal surface were measured.

Substitutions	Site	Amount(%)	Sn-content (%)
Cr	Mn-site	4.4 ± 0.9	0.7 ± 0.5
Fe	Mn-site	9.9 ± 0.5	0.6 ± 0.1
Fe*	Mn-site	91.3 ± 0.9	2.7 ± 0.3
		91.6 ± 0.9	1.9 ± 0.1
Co	Mn-site	0.2 ± 0.3	0.2 ± 0.1
Ni	Mn-site	0.1 ± 0.2	”0”
Cu	Mn-site	0.5 ± 0.3	0.5 ± 0.1
Ru	Mn-site	0.2 ± 0.9	“0”
Rh	Mn-site	0.2 ± 0.3	“0”
Pd	Mn-site	“0”	0.4 ± 0.1
Re	Mn-site	“0”	0.3 ± 0.3
Pt	Mn-site	“0”	0.5 ± 0.3
Sb	As-site	2.6 ± 0.3	0.3 ± 0.2

0.05 mm diameter Pt electrical leads to the samples were made using silver epoxy for the polycrystalline samples and $\text{In}_{98}\text{Ag}_2$ solder for the crystals. The measurement current amplitude and frequency were 1 mA and 38 Hz for the polycrystalline samples, and 0.01 mA and 38 Hz and 18 Hz for the Fe- and Cr-doped crystals, respectively. The room-temperature contact resistances were 4–5 Ω for the quenched polycrystalline $\text{Ba}(\text{Mn}_{0.8}\text{Fe}_{0.2})_2\text{As}_2$ and $\text{Ba}(\text{Mn}_{0.2}\text{Fe}_{0.8})_2\text{As}_2$ samples and 0.1 and 1 k Ω for the Cr- and Fe-doped BaMn_2As_2 crystals, respectively. The validity of the resistivity data was verified by examining the voltage waveform at representative temperatures for each sample.

III. MISCIBILITY GAP IN THE $\text{Ba}(\text{Mn}_x\text{Fe}_{1-x})_2\text{As}_2$ SYSTEM

A. Slow-Cooled Polycrystalline Samples

A room-temperature XRD pattern of a slow-cooled sample of $\text{Ba}(\text{Mn}_{0.8}\text{Fe}_{0.2})_2\text{As}_2$ is shown in Fig. 1(a). The XRD data for the sample indicate that the sample contains a significant amount of impurities, mainly $\text{Fe}_{1-x}\text{Mn}_x\text{As}$. We refined the XRD data using a two-phase (BaMn_2As_2 -rich and BaFe_2As_2 -rich phases) Rietveld refinement but did not include the impurity phases in the refinement. For each 122-type phase, the data were refined in the body-centered-tetragonal space group $I4/mmm$ using the atomic positions of the ThCr_2Si_2 -type structure.² Figure 1(a) shows the Rietveld fit, the difference profile between the data and fit, and the fitted line positions. The room temperature powder XRD pattern of the slow-cooled sample of $\text{Ba}(\text{Mn}_{0.2}\text{Fe}_{0.8})_2\text{As}_2$ is shown in Fig. 2(a). Similar to the case of $\text{Ba}(\text{Mn}_{0.8}\text{Fe}_{0.2})_2\text{As}_2$ in Fig. 1(a), the slow-cooled sample of $\text{Ba}(\text{Mn}_{0.2}\text{Fe}_{0.8})_2\text{As}_2$ contains a significant amount of impurities. A two-phase Rietveld refinement of the data was carried out in the same way as for $\text{Ba}(\text{Mn}_{0.8}\text{Fe}_{0.2})_2\text{As}_2$ to obtain the unit cell parameters and the volumes and percentage molar fractions of BaMn_2As_2 -rich and BaFe_2As_2 -rich phases. This fit is shown in Fig. 2(a).

Similar to the above cases of $\text{Ba}(\text{Mn}_{0.8}\text{Fe}_{0.2})_2\text{As}_2$ and $\text{Ba}(\text{Mn}_{0.2}\text{Fe}_{0.8})_2\text{As}_2$, the slow-cooled samples of $\text{Ba}(\text{Mn}_{1-x}\text{Fe}_x)_2\text{As}_2$ ($x = 0.4, 0.5$ and 0.6) also contain phase-separated mixtures of the Fe-rich and Mn-rich 122-type phases together with impurity phases. We carried out similar two-phase Rietveld refinements of the XRD patterns of these samples for the Mn-rich and Fe-rich 122-type phases. The a and c lattice parameters and the unit cell volumes of the BaMn_2As_2 -rich and BaFe_2As_2 -rich phases in $\text{Ba}(\text{Mn}_x\text{Fe}_{1-x})_2\text{As}_2$ are listed in Table II and plotted versus nominal Mn content x for all five samples in Fig. 3, together with data² for $x = 0$ and $x = 1$ from the literature. The corresponding volume and molar fraction of the BaMn_2As_2 -rich phase in the samples are plotted versus nominal Mn concentration x in Fig. 4. Since impurity phases were not accounted for in the refinements, the values of the molar fraction in Fig. 4 represent the relative fractions of the BaMn_2As_2 -rich and BaFe_2As_2 -rich phases.

Considering Vegard’s law shown in Fig. 3 and the straight-line fit to the data in Fig. 4, the data in these two figures

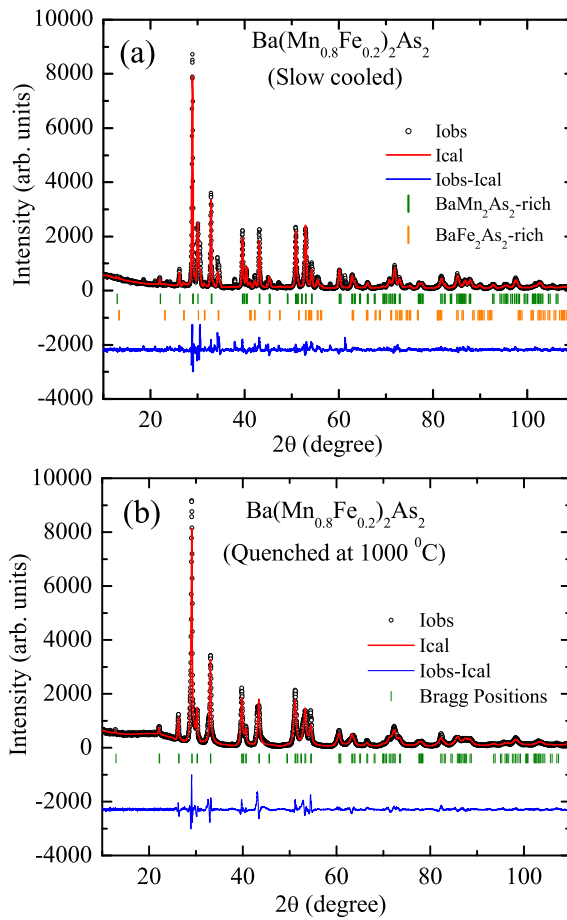


FIG. 1: (Color online) (a) Room-temperature powder XRD pattern (open circles) of a slow-cooled sample of $\text{Ba}(\text{Mn}_{0.8}\text{Fe}_{0.2})_2\text{As}_2$. The solid line is a two-phase (BaMn_2As_2 -rich and BaFe_2As_2 -rich phases) Rietveld refinement fit. Difference profile and Bragg positions of both the phase are also shown. (b) Room temperature powder XRD pattern (open circle) of a quenched (1000 °C to 77 K) sample of $\text{Ba}(\text{Mn}_{0.8}\text{Fe}_{0.2})_2\text{As}_2$, along with the Rietveld fit, difference profile and Bragg peak positions.

consistently indicate that a miscibility gap occurs in the $\text{Ba}(\text{Mn}_x\text{Fe}_{1-x})_2\text{As}_2$ system at 300 K (for the slow-cooled samples) that has the composition range $0.12 \lesssim x \lesssim 1$. That is, about 12% of Mn can be substituted for Fe in BaFe_2As_2 but almost no Fe can be substituted for Mn in BaMn_2As_2 . In the following section we investigate whether the miscibility gap boundaries are temperature-dependent.

B. Quenched Polycrystalline Samples

The Rietveld refinement of the powder XRD data for a $\text{Ba}(\text{Mn}_{0.8}\text{Fe}_{0.2})_2\text{As}_2$ sample quenched from 1000 °C to 77 K, shown in Fig. 1(b), indicates that the sample is a single phase, with no evidence of phase separation of different compositions of 122-type phases or of impurity phases. The unit cell volume calculated from the lattice parameters is $229.11(3) \text{ \AA}^3$, which is 2.19% smaller than that of pure BaMn_2As_2 . Similarly, Rietveld refinement of a quenched $\text{Ba}(\text{Mn}_{0.2}\text{Fe}_{0.8})_2\text{As}_2$ sample shown in Fig. 2(b) exhibits an excellent fit to the data for a single 122-type phase with no evidence for any impurity phases. The volume of the unit cell is $210.06(1) \text{ \AA}^3$, which is 2.78% larger than that of pure BaFe_2As_2 , as expected for a single-phase sample. These observations and those above in Sec. III A demonstrate that BaMn_2As_2 and BaFe_2As_2 are miscible at 1000 °C at the compositions $\text{Ba}(\text{Mn}_{0.8}\text{Fe}_{0.2})_2\text{As}_2$ and $\text{Ba}(\text{Mn}_{0.2}\text{Fe}_{0.8})_2\text{As}_2$ but phase-separate when slowly cooled from this temperature.

In contrast to the samples with compositions $x = 0.2$ and 0.8 that were single-phase when quenched from 1000 °C to 77 K, the samples with $x = 0.4, 0.5$ and 0.6 synthesized under identical conditions were manifestly multi-phase, demonstrating that the miscibility gap at 1000 °C is $0.2 \lesssim x \lesssim 0.8$. The x-ray patterns of the latter three compositions

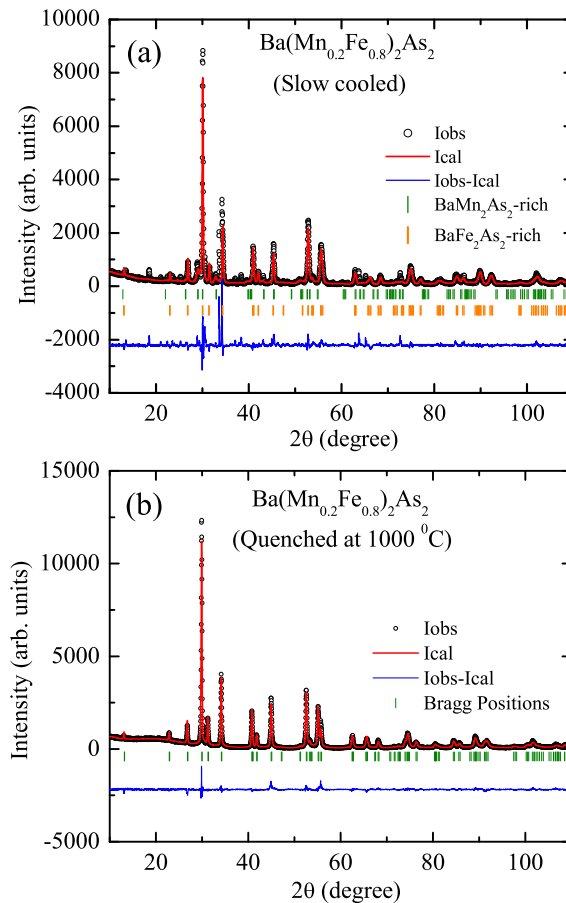


FIG. 2: (Color online) (a) Room temperature powder XRD pattern (open circles) of a slow-cooled sample of $\text{Ba}(\text{Mn}_{0.2}\text{Fe}_{0.8})_2\text{As}_2$. The solid line is a two-phase (BaMn_2As_2 -rich and BaFe_2As_2 -rich phases) Rietveld refinement. The difference profile and Bragg peak positions of both phases are also shown. (b) Room-temperature powder XRD pattern (open circles) of a single-phase sample of $\text{Ba}(\text{Mn}_{0.2}\text{Fe}_{0.8})_2\text{As}_2$ obtained by quenching from 1000 °C to 77 K, along with the Rietveld refinement fit, difference profile and Bragg peak positions.

were too ill-defined to be able to obtain reliable Rietveld refinements using them. On increasing the temperature to 1100–1400 °C from which the samples were quenched (see Table II), multi-phase samples were still obtained but for which the x-ray patterns could be refined assuming an approximately single 122-type phase plus impurity phases, suggesting that the miscibility gap does not close even at 1400 °C. For example, shown in Fig. 5 are powder XRD data for $\text{Ba}(\text{Mn}_{0.5}\text{Fe}_{0.5})_2\text{As}_2$ samples that were either slow-cooled from 1000 °C or quenched from 1400 °C as representative of the $x = 0.4, 0.5$ and 0.6 compositions. Both samples contain impurity phases which are mainly FeAs_2 and $\text{Fe}_{1-x}\text{Mn}_x\text{As}$. A two-phase Rietveld refinement of the XRD data for the slow-cooled sample in Fig. 5(a) yields the unit cell volumes and percentage molar fractions of BaMn_2As_2 -rich and BaFe_2As_2 -rich phases shown in Table I and Figs. 3 and 4 that were discussed above in Sec. III A. The powder XRD pattern of the quenched sample in Fig. 5(b) indicates that the sample contains an approximately single 122-type phase in addition to impurity phases. The calculated unit cell volume of the 122-type phase is $225.74(5) \text{ \AA}^3$, which suggests a significant mixing of BaMn_2As_2 and BaFe_2As_2 at 1400 °C, but as noted this sample is not single-phase. The crystal data for these quenched samples with compositions $x = 0.4, 0.5$ and 0.6 are summarized in Table II and Figs. 3 and 4.

The results in this section indicate that the miscibility gap $0.12 \lesssim x \lesssim 1$ at 300 K has narrowed to $0.2 \lesssim x \lesssim 0.8$ at 1000 °C. The occurrence of a single 122-type phase plus impurity phases for samples with $0.2 \lesssim x \lesssim 0.8$ quenched from 1100–1400 °C suggest the existence of a homogeneity range at these temperatures for the 122-type phase.

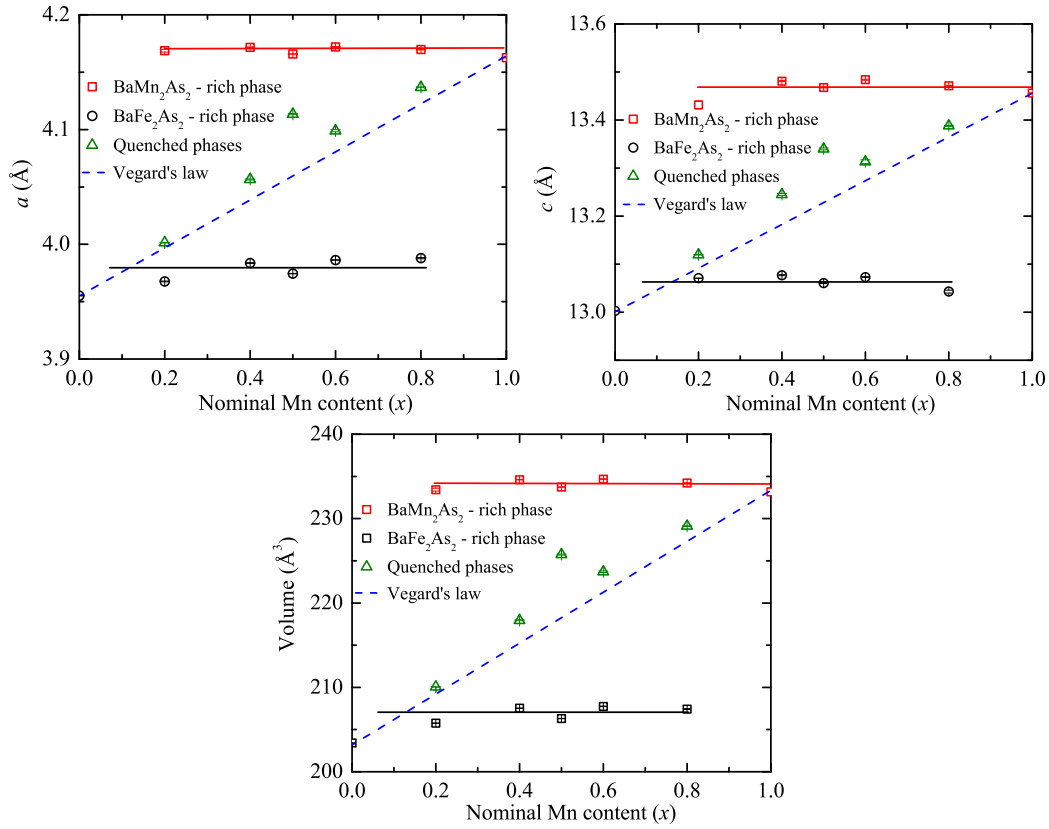


FIG. 3: (Color online) Variations of the tetragonal lattice parameters a and c and of the unit cell volumes for the BaMn_2As_2 -rich and BaFe_2As_2 -rich phases present in slow-cooled polycrystalline samples of $\text{Ba}(\text{Mn}_x\text{Fe}_{1-x})_2\text{As}_2$ versus the nominal Mn concentration x . These data indicate the presence of a miscibility gap in the composition range $0.12 \lesssim x \lesssim 1$ at 300 K. Also shown are data for quenched samples, within which only the $x = 0.2$ and $x = 0.8$ samples were single-phase. Error bars are appended to the data points and are smaller than the size of the symbols.

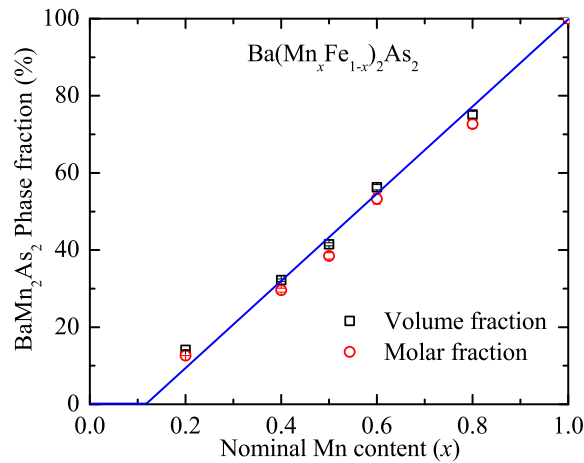


FIG. 4: (Color online) Volume and molar fractions of the BaMn_2As_2 -rich phase as a function of nominal Mn concentration x in slow-cooled samples of polycrystalline $\text{Ba}(\text{Mn}_x\text{Fe}_{1-x})_2\text{As}_2$. The straight-line fit indicates that the miscibility gap at 300 K has the composition range $0.12 \lesssim x \lesssim 1$, consistent with the crystal data in Fig. 3.

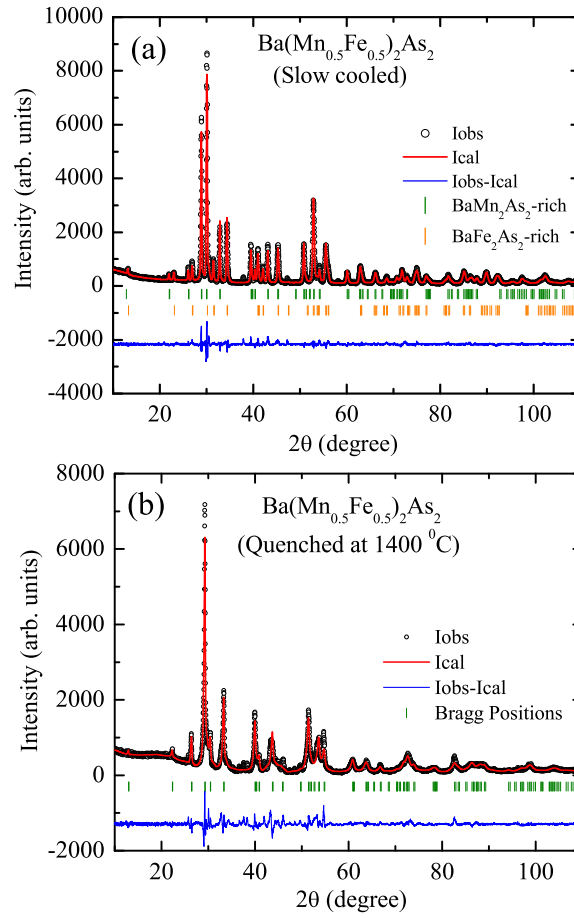


FIG. 5: (Color online) Room-temperature powder XRD patterns (open circles) of (a) a slow-cooled sample of $\text{Ba}(\text{Mn}_{0.5}\text{Fe}_{0.5})_2\text{As}_2$ and (b) a $\text{Ba}(\text{Mn}_{0.5}\text{Fe}_{0.5})_2\text{As}_2$ sample quenched from 1400°C to 77 K . The solid curve in (a) is a two-phase (BaMn_2As_2 -rich and BaFe_2As_2 -rich 122-type phases) Rietveld refinement fit whereas in (b) only a single 122-type phase is seen. Difference profiles and Bragg peak positions of the fitted phases are also shown. Bragg peaks from impurity phases which are mainly $\text{Fe}_{1-x}\text{Mn}_x\text{As}$ and FeAs_2 are also seen in the XRD patterns for both samples.

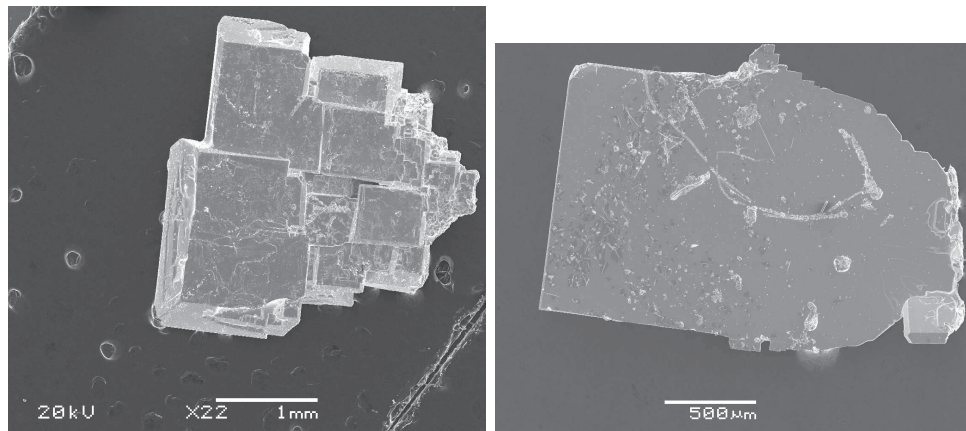


FIG. 6: Scanning electron micrographs of $\text{Ba}(\text{Mn}_x\text{Fe}_{1-x})_2\text{As}_2$ crystals grown in Sn flux from a starting composition of $\text{Ba}(\text{Mn}_{0.5}\text{Fe}_{0.5})_2\text{As}_2$ upon slowly cooling from 1100°C . The top picture shows “Crystal-2” which contains intergrowths of crystals with compositions as listed for Crystal-2 in Table III for which the decanting temperature was 700°C . The bottom picture is of a large single crystal “Crystal-8” (and a small crystal of the same composition attached to it on the bottom right) with the composition given for Crystal-8 in Table III) for which the decanting temperature was 900°C . In both pictures, the large flat surfaces in the foreground are the ab planes of the crystals.

TABLE II: Crystal data at room temperature for the 122-type phase(s) in slow-cooled (SC) and quenched (Q) phases of polycrystalline $\text{Ba}(\text{Mn}_x\text{Fe}_{1-x})_2\text{As}_2$ ($x = 0.2, 0.4, 0.5, 0.6$ and 0.8). All samples except for the quenched $\text{Ba}(\text{Mn}_{0.2}\text{Fe}_{0.8})_2\text{As}_2$ and $\text{Ba}(\text{Mn}_{0.8}\text{Fe}_{0.2})_2\text{As}_2$ samples also contained impurity phases. The temperature in parentheses following a “Q” symbol is the temperature from which the sample was quenched. The crystal data were obtained from Rietveld refinements of powder XRD data in the body-centered-tetragonal space group $I4/mmm$ using the atomic positions of the ThCr_2Si_2 -type structure.² The tetragonal lattice parameters are a and c and V_{cell} is the unit cell volume. M represents transition metal atoms (Mn and Fe), z_{As} is the c -axis position parameter of As, $d_{M-\text{As}}$ is the Mn/Fe-As bond distance and θ_2 is the twofold As- M -As bond angle² within a distorted M -centered $M\text{As}_4$ tetrahedron.

Compound	SC or Q	a (Å)	c (Å)	V_{cell} (Å ³)	z_{As}	$d_{M-\text{As}}$ (Å)	θ_2 (deg)
$\text{Ba}(\text{Mn}_{0.2}\text{Fe}_{0.8})_2\text{As}_2$	Q (1000 °C)	4.0014(1)	13.1195(5)	210.06(1)	0.3566(1)	2.441(2)	110.1(1)
	SC (Phase-1)	4.169(1)	13.432(8)	233.4(2)	0.358(1)	2.54(2)	110(1)
	SC (Phase-2)	3.9676(3)	13.071(1)	205.76(3)	0.3550(2)	2.412(3)	110.7(2)
$\text{Ba}(\text{Mn}_{0.4}\text{Fe}_{0.6})_2\text{As}_2$	Q (1100 °C)	4.0565(4)	13.245(2)	217.95(5)	0.3577(2)	2.480(4)	109.8(2)
	SC (Phase-1)	4.1716(3)	13.481(1)	234.60(3)	0.3619(3)	2.574(5)	108.3(3)
	SC (Phase-2)	3.9837(2)	13.0770(7)	207.53(2)	0.3562(2)	2.428(2)	110.2(2)
$\text{Ba}(\text{Mn}_{0.5}\text{Fe}_{0.5})_2\text{As}_2$	Q (1400 °C)	4.1135(5)	13.340(2)	225.74(5)	0.3599(2)	2.526(4)	109.0(2)
	SC (Phase-1)	4.1659(2)	13.4679(7)	233.74(2)	0.3614(2)	2.567(3)	108.5(2)
	SC (Phase-2)	3.9744(2)	13.0605(7)	206.30(2)	0.3554(1)	2.417(2)	110.6(1)
$\text{Ba}(\text{Mn}_{0.6}\text{Fe}_{0.4})_2\text{As}_2$	Q (1250 °C)	4.099(1)	13.313(4)	223.7(1)	0.3584(3)	2.507(6)	109.7(3)
	SC (Phase-1)	4.1719(3)	13.484(1)	234.68(3)	0.3620(2)	2.575(4)	108.2(2)
	SC (Phase-2)	3.9863(3)	13.073(1)	207.74(3)	0.3555(3)	2.424(5)	110.6(3)
$\text{Ba}(\text{Mn}_{0.8}\text{Fe}_{0.2})_2\text{As}_2$	Q (1000 °C)	4.1368(3)	13.388(1)	229.11(3)	0.3615(1)	2.551(2)	108.4(1)
	SC (Phase-1)	4.1697(3)	13.4714(9)	234.22(3)	0.3626(2)	2.578(4)	107.9(2)
	SC (Phase-2)	3.9880(5)	13.043(3)	207.43(6)	0.3567(5)	2.432(8)	110.2(5)

C. $\text{Ba}(\text{Mn}_x\text{Fe}_{1-x})_2\text{As}_2$ Single Crystals

Two batches of $\text{Ba}(\text{Mn}_x\text{Fe}_{1-x})_2\text{As}_2$ crystals were grown in Sn flux from a polycrystalline sample of nominal composition $\text{Ba}(\text{Mn}_{0.5}\text{Fe}_{0.5})_2\text{As}_2$ by slowly cooling from 1100 °C as discussed in Sec. II. The molten Sn flux was decanted at either 700 or 900 °C by removing the silica tube from the oven at the respective temperature and quickly placing the inverted tube into a centrifuge that spun up within ~ 10 s. This procedure is equivalent to a slow quench of the crystals to room temperature from the respective temperature. Examples of such crystals are shown in Fig. 6. The compositions of many crystals from the two batches at up to six points on each crystal were measured using EDX and representative results are shown in Table III. The data for the crystals examined demonstrate that a miscibility gap exists in the $\text{Ba}(\text{Mn}_x\text{Fe}_{1-x})_2\text{As}_2$ system, with a composition range of $0.16 \lesssim x \lesssim 0.93$ at 700 °C and an upper limit to x that decreases somewhat to $x_{\text{max}} \approx 0.89$ at 900 °C, qualitatively similar to our results above on polycrystalline samples. Note that Crystal-3 obtained by decanting the Sn flux at 700 °C showed a $\sim \pm 30\%$ variation in the composition at different points on the crystal.

Among eleven crystals for which the Sn flux was decanted at 900 °C that were examined by EDX analysis (only five of which are shown in Table III), none were found to be Fe-rich even though such crystals were found when the Sn flux was decanted at 700 °C. This difference suggests that Fe-rich crystals grow in Sn flux only between 700 and 900 °C when the starting composition is $\text{Ba}(\text{Mn}_{0.5}\text{Fe}_{0.5})_2\text{As}_2$.

IV. PHYSICAL PROPERTIES OF SINGLE-PHASE QUENCHED POLYCRYSTALLINE $\text{Ba}(\text{Mn}_x\text{Fe}_{1-x})_2\text{As}_2$ SAMPLES ($x = 0.2, 0.8$)

A. Electrical Resistivity Measurements

The $\rho(T)$ data for the single-phase quenched polycrystalline samples of $\text{Ba}(\text{Mn}_{0.8}\text{Fe}_{0.2})_2\text{As}_2$ and $\text{Ba}(\text{Mn}_{0.2}\text{Fe}_{0.8})_2\text{As}_2$ are shown in Fig. 7. The large magnitudes and semiconducting-like temperature dependences suggest nonmetallic ground states for both compounds. However, we emphasize that electronic transport measurements on polycrystalline samples can give spurious results. Measurements on single crystals are needed for definitive electronic transport

TABLE III: Mn and Fe contents of $\text{Ba}(\text{Mn}_x\text{Fe}_{1-x})_2\text{As}_2$ single crystals grown from a polycrystalline sample of nominal composition $\text{Ba}(\text{Mn}_{0.5}\text{Fe}_{0.5})_2\text{As}_2$ using Sn flux that was decanted using a centrifuge at either 700 or 900 °C, as listed, equivalent to a slow quench to room temperature from the respective temperature. The chemical composition was determined at up to six basal-plane spots on each crystal, as listed, using EDX analysis. Of eleven crystals examined for which the Sn was decanted at 900 °C (only five such crystals are shown in the table), none were found to be Fe-rich. Note that “Crystal-2” is an intergrowth of Mn-rich and Fe-rich crystals shown in the top panel of Fig. 6.

Crystal	Spot	Mn-content x (%)	Fe-content $100 - x$ (%)
Crystal-1 (700 °C)	1	8.7 ± 0.9	Remainder
	2	8.4 ± 0.9	Remainder
Crystal-2 (700 °C)	1	8.0 ± 0.9	Remainder
	2	Remainder	6.2 ± 0.6
	3	Remainder	6.9 ± 0.6
	4	9 ± 1	Remainder
Crystal-3 (700 °C)	1	10.4 ± 0.6	Remainder
	2	8 ± 1	Remainder
	3	10 ± 1	Remainder
	4	9 ± 1	Remainder
	5	16 ± 1	Remainder
	6	15 ± 1	Remainder
Crystal-4 (900 °C)	1	Remainder	9.7 ± 0.6
	2	Remainder	10.5 ± 0.5
	3	Remainder	9.7 ± 0.5
	4	Remainder	9.8 ± 0.5
Crystal-5 (900 °C)	1	Remainder	8.8 ± 0.5
	2	Remainder	9.2 ± 0.5
	3	Remainder	7.9 ± 0.5
Crystal-6 (900 °C)	1	Remainder	10.8 ± 0.5
	2	Remainder	10.4 ± 0.9
	3	Remainder	11.3 ± 0.5
Crystal-7 (900 °C)	1	Remainder	9.8 ± 0.5
	2	Remainder	9.1 ± 0.5
	3	Remainder	10.1 ± 0.5
Crystal-8 (900 °C)	1	Remainder	11.1 ± 0.6
	2	Remainder	10.2 ± 0.9
	3	Remainder	8.5 ± 0.5

characterizations. The $\rho(T)$ data in applied magnetic fields $H = 0$ and $H = 8$ T closely superimpose, suggesting that spin-dependent scattering does not contribute significantly to the resistivity of these materials over the T range of the measurements. Plots of $\ln\rho$ versus $1/T$ are shown in the insets of the respective figures. Extended linear regions are not found in these plots, which precludes the estimation of activation energies Δ in contrast to BaMn_2As_2 crystals where $\Delta \sim 30$ meV was found from in-plane $\rho(T)$ measurements.¹⁵

The $\rho(T)$ data for Fe-rich $\text{Ba}(\text{Mn}_{0.2}\text{Fe}_{0.8})_2\text{As}_2$ in Fig. 7(b) show no obvious anomaly that might arise from a structural and/or antiferromagnetic (or spin density wave SDW) transition below 300 K. We note that the results in Ref. 12 for single crystals of the $\text{Ba}(\text{Mn}_x\text{Fe}_{1-x})_2\text{As}_2$ system with $0 \leq x \leq 0.176$ show evidence for stripe SDW order for $x = 0.176$ below a possibly smeared-out Néel temperature $T_N \sim 200$ K [see Fig. 4(a) in Ref. 12] and with a $T = 0$ ordered moment of $0.6 \mu_B$ per transition metal atom. On the other hand, our $\rho(T)$ data in Fig. 7(a) for $\text{Ba}(\text{Mn}_{0.8}\text{Fe}_{0.2})_2\text{As}_2$, near the opposite Mn-rich end of the composition range, suggest that some type of phase transition may occur at $T \approx 260$ K.

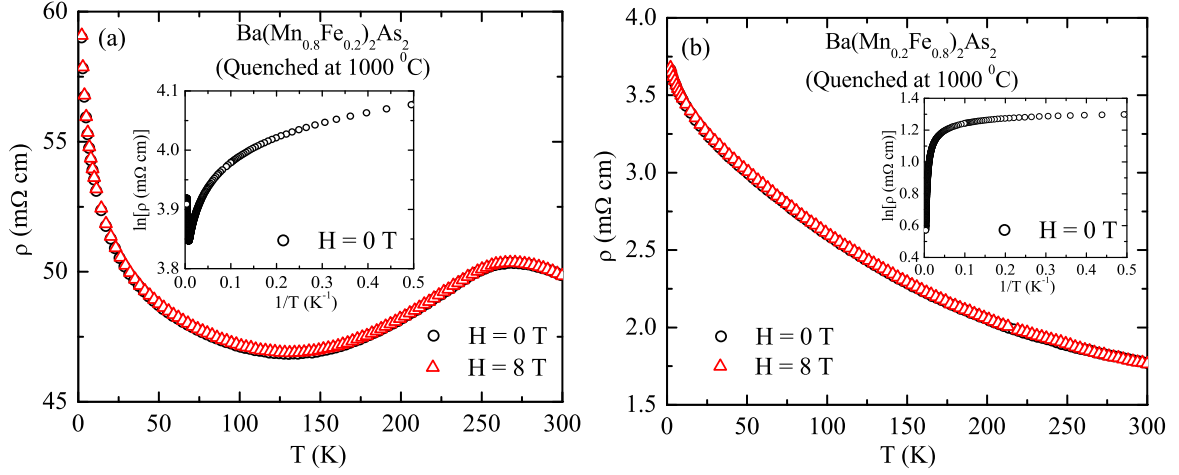


FIG. 7: (Color online) Electrical resistivity ρ of single-phase quenched polycrystalline samples of (a) $\text{Ba}(\text{Mn}_{0.8}\text{Fe}_{0.2})_2\text{As}_2$ and (b) $\text{Ba}(\text{Mn}_{0.2}\text{Fe}_{0.8})_2\text{As}_2$ versus temperature T measured in applied magnetic fields $H = 0$ and 8 T. Insets: $\ln\rho$ versus $1/T$.

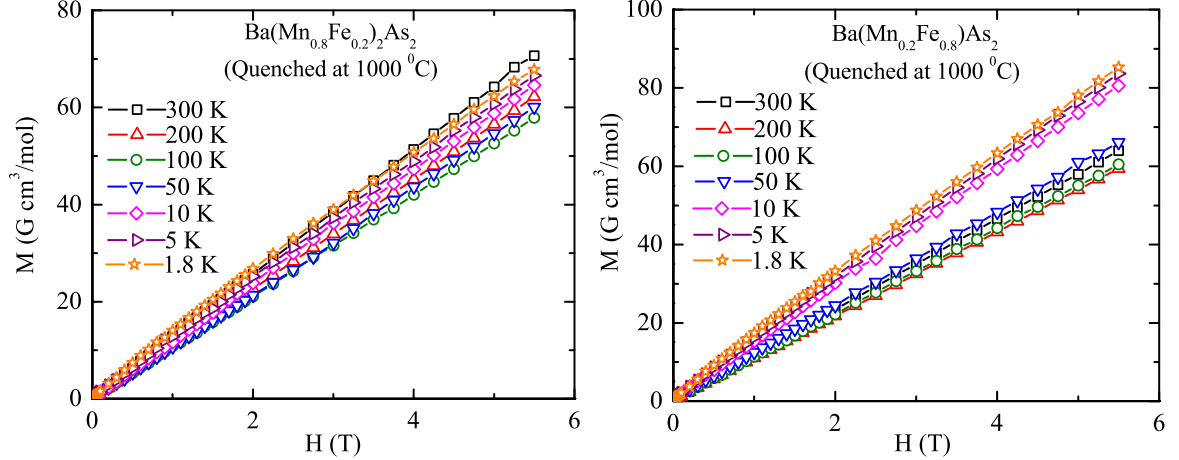


FIG. 8: (Color online) Magnetization M versus applied magnetic field H isotherms at the indicated temperatures for single-phase polycrystalline $\text{Ba}(\text{Mn}_{0.8}\text{Fe}_{0.2})_2\text{As}_2$ (top panel) and $\text{Ba}(\text{Mn}_{0.2}\text{Fe}_{0.8})_2\text{As}_2$ (bottom panel). The solid lines are guides to the eye.

B. Magnetization and Magnetic Susceptibility Measurements

Isothermal magnetization M versus H measurements for the quenched single-phase polycrystalline samples of $\text{Ba}(\text{Mn}_{0.8}\text{Fe}_{0.2})_2\text{As}_2$ and $\text{Ba}(\text{Mn}_{0.2}\text{Fe}_{0.8})_2\text{As}_2$ are shown in Fig. 8 for the field range up to 5.5 T. The M data taken at various temperatures for both compositions are proportional to H , except for the data below 10 K where they exhibit slight nonlinear behaviors with negative curvature for fields below ~ 2 T, which most likely arise from saturable paramagnetic impurities. We performed linear fits to the $M(H)$ data in the field range $3 \leq H \leq 5.5$ T for $T \leq 10$ K; the high-field slopes give independent values of $\chi(T)$ of the materials below 10 K that are referred to below.

The magnetic susceptibilities $\chi \equiv M/H$ versus temperature T measured in $H = 3$ T for the quenched samples of $\text{Ba}(\text{Mn}_{0.8}\text{Fe}_{0.2})_2\text{As}_2$ and $\text{Ba}(\text{Mn}_{0.2}\text{Fe}_{0.8})_2\text{As}_2$ are shown in Fig. 9, together with the values of the $\chi(T)$ calculated as described above from the $M(H)$ isotherms for $T \leq 10$ K. These latter values are similar to the values obtained in the respective $M(T)$ scans at fixed H , demonstrating that the amounts of saturable impurities are almost negligible in these samples. The positive slopes of $\chi(T)$ for $\text{Ba}(\text{Mn}_{0.8}\text{Fe}_{0.2})_2\text{As}_2$ and $\text{Ba}(\text{Mn}_{0.2}\text{Fe}_{0.8})_2\text{As}_2$ at the higher temperatures are consistent with the similar behaviors reported in the paramagnetic states for single crystals of BaMn_2As_2 (Ref. 15) and BaFe_2As_2 .^{26,28} The upturns in $\chi(T)$ for the samples below ~ 70 – 200 K may be due to the presence of nonsaturable paramagnetic impurities and/or magnetic defects, although as previously noted we did not detect any impurity phases in these samples from XRD measurements. There is no clear evidence from the $\chi(T)$ data for either sample for an

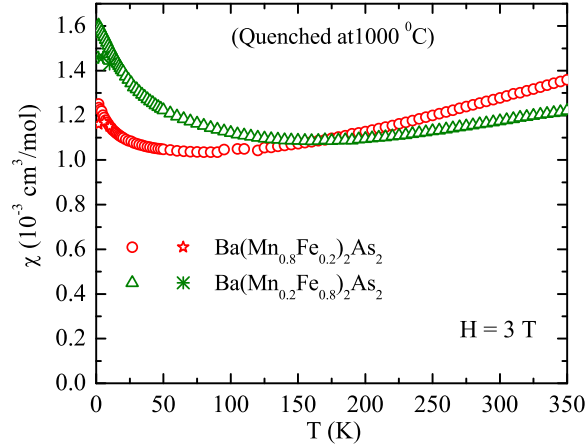


FIG. 9: (Color online) Magnetic susceptibility $\chi \equiv M/H$ versus temperature T of single-phase quenched polycrystalline $\text{Ba}(\text{Mn}_{0.8}\text{Fe}_{0.2})_2\text{As}_2$ and $\text{Ba}(\text{Mn}_{0.2}\text{Fe}_{0.8})_2\text{As}_2$ samples measured in an applied magnetic field $H = 3$ T. Stars and asterisks represent the low-temperature χ values extracted at $T \leq 10$ K from $M(H)$ isotherms for these two compounds, respectively.

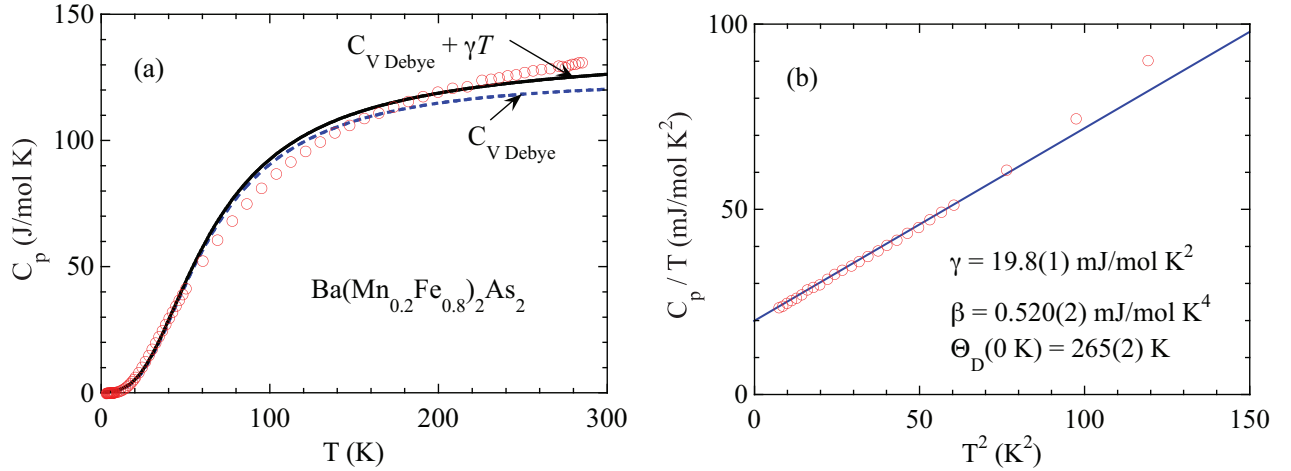


FIG. 10: (Color online) (a) Heat capacity C_p versus temperature T (open circles) for a single-phase polycrystalline sample of $\text{Ba}(\text{Mn}_{0.2}\text{Fe}_{0.8})_2\text{As}_2$ quenched from 1000°C . Also shown are the Debye lattice heat capacity function $C_{V \text{ Debye}}(T)$ obtained from Eq. (3), and $C_{V \text{ Debye}}(T) + \gamma T$, where the parameters are the Debye temperature $\Theta_D = 265$ K and γ value determined from the low-temperature fit by Eq. (1) in (b).

anomaly in $\chi(T)$ due a spin density wave (SDW) and/or tetragonal-to-orthorhombic transition. Such transitions are observed at ≈ 137 K in undoped BaFe_2As_2 .^{26,28}

We note that consistent with the XRD data in Fig. 5(b) for the quenched (1400°C to 77 K) sample of $\text{Ba}(\text{Mn}_{0.5}\text{Fe}_{0.5})_2\text{As}_2$, our $M(H, T)$ data for this sample (not shown) indicated the presence of a substantial amount of ferromagnetic impurities. Hence, we did not attempt to extract $\chi(T)$ from the $M(H, T)$ data for this sample.

C. Heat Capacity Measurements

The temperature variation of the heat capacity at constant pressure (C_p) for the two single-phase quenched polycrystalline samples of $\text{Ba}(\text{Mn}_{0.2}\text{Fe}_{0.8})_2\text{As}_2$ and $\text{Ba}(\text{Mn}_{0.8}\text{Fe}_{0.2})_2\text{As}_2$ are shown in Figs. 10 and 11, respectively. The measured value of C_p at $T = 275$ K is 129 and 130 J/mol K for $\text{Ba}(\text{Mn}_{0.2}\text{Fe}_{0.8})_2\text{As}_2$ and $\text{Ba}(\text{Mn}_{0.8}\text{Fe}_{0.2})_2\text{As}_2$, respectively. These values are close to, but a bit larger than, the classical Dulong-Petit heat capacity $C_V = 15R \approx 124.7$ J/mol K expected for a crystalline compound containing five atoms/formula unit. The $C_p(T)$ data for the two compounds show no evidence for any phase transitions in the temperature range of measurement.

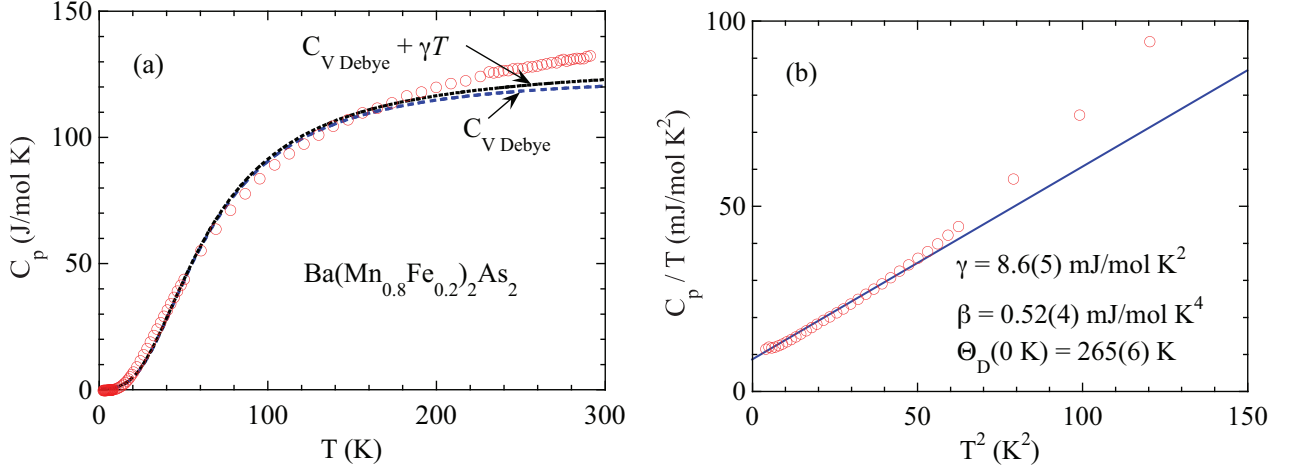


FIG. 11: (Color online) The same types of heat capacity plots for $\text{Ba}(\text{Mn}_{0.8}\text{Fe}_{0.2})_2\text{As}_2$ quenched from 1000°C as for $\text{Ba}(\text{Mn}_{0.2}\text{Fe}_{0.8})_2\text{As}_2$ in Fig. 10.

We fitted the low-temperature $C_p(T)$ data in Figs. 10(b) and 11(b) using the expression

$$\frac{C_p}{T} = \gamma + \beta T^2 \quad (1)$$

where γ is the Sommerfeld coefficient of the electronic heat capacity and β is the coefficient of the Debye T^3 term for lattice heat capacity. The values of the fitting parameters and their error bars are given in the figures. The value of γ reported by Singh et al. for BaMn_2As_2 is $0.0(4)$ mJ/mol K^2 .¹⁵ The nonzero values of γ for $\text{Ba}(\text{Mn}_{0.8}\text{Fe}_{0.2})_2\text{As}_2$ and $\text{Ba}(\text{Mn}_{0.2}\text{Fe}_{0.8})_2\text{As}_2$ suggest metallic ground states. Indeed, our $\rho(T)$ measurements indicate that the magnitude of the resistivities of $\text{Ba}(\text{Mn}_{0.8}\text{Fe}_{0.2})_2\text{As}_2$ and $\text{Ba}(\text{Mn}_{0.2}\text{Fe}_{0.8})_2\text{As}_2$ are significantly smaller than reported for BaMn_2As_2 .¹⁵ The Debye temperature Θ_D is estimated using the expression²⁹

$$\Theta_D = \left(\frac{12\pi^4 R n}{5\beta} \right)^{1/3} \quad (2)$$

where n is the number of atoms per formula unit [$n = 5$ in the present case of $\text{Ba}(\text{Mn}_x\text{Fe}_{1-x})_2\text{As}_2$] and R is the molar gas constant. The calculated values of Θ_D are about 265 K, somewhat larger than $\Theta_D = 246(4)$ K reported for a single crystal of BaMn_2As_2 .¹⁵

The Debye lattice heat capacity function at constant volume per mole of atoms is Kittel2005

$$C_{\text{Debye } V} = 9R \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^4}{(e^x - 1)^2} dx. \quad (3)$$

This function describes the heat capacity of acoustic phonons. The $C_{\text{Debye } V}(T)$ is plotted in Figs. 10(a) and 11(a) using the value $\Theta_D = 265$ K determined in Figs. 10(b) and 11(b) and taking into account the five atoms per formula unit. Overall, the Debye function fits the data reasonably well, but a temperature dependence of Θ_D is evident from the comparison.³⁰ Also, the experimental data at the higher temperatures are above the Debye function, suggesting additional contributions. We added the respective electronic contributions γT to the Debye function, as shown in Figs. 10(a) and 11(a). The data are still above the calculated values at the highest temperatures. Finally, we calculated the difference $C_p - C_V$ for the lattice heat capacity for the compound BaFe_2As_2 according to the thermodynamic relation

$$C_p - C_V = V_M \beta^2(T) B(T) T,$$

where V_M is the molar volume, β is the volume thermal expansion coefficient, and B is the bulk modulus. For the 200–300 K temperature range, using the values $\beta \approx 4.8 \times 10^{-5} \text{ K}^{-1}$,³¹ $B = 66 \times 10^{11} \text{ dyne/cm}^2$,³² and $V_M = 61.5 \text{ cm}^3/\text{mol}$,² we obtained

$$C_p - C_V \approx \left(9.3 \frac{\text{mJ}}{\text{mol K}^2} \right) T. \quad (200 \text{ to } 300 \text{ K})$$

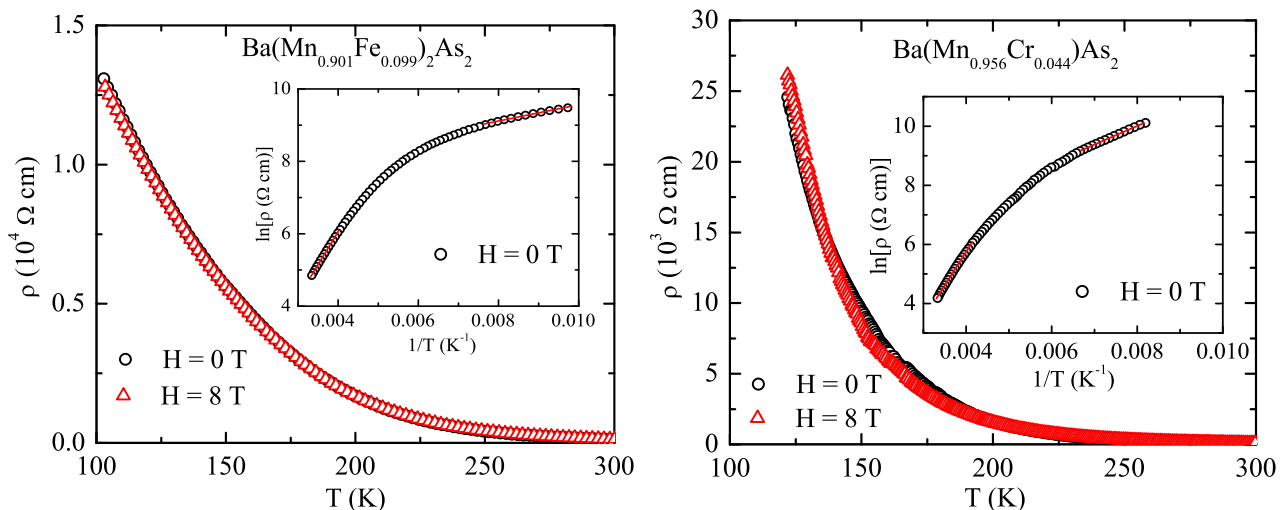


FIG. 12: (Color online) In-plane electrical resistivity ρ versus temperature T of single crystals of $\text{Ba}(\text{Mn}_{0.901}\text{Fe}_{0.099})_2\text{As}_2$ (top panel) and $\text{Ba}(\text{Mn}_{0.956}\text{Cr}_{0.044})_2\text{As}_2$ (bottom panel) in applied magnetic fields $H = 0$ and 8 T. Inset of each panel: $\ln\rho$ versus $1/T$ at $H = 0$ T. The two solid lines in the upper inset are fits of the data by the expression $\ln\rho = A + \Delta/T$ over the temperature ranges 100–130 K and 250–300 K, which yield activation energies $\Delta = 19$ and 156 meV, respectively. In the lower inset, the data were fitted from 120–150 K and 250–300 K, as shown, yielding $\Delta = 54$ and 197 meV, respectively.

This prediction is similar in magnitude to the electronic γT contribution for the Mn-rich sample in Fig. 11(a) and is not sufficient to obtain agreement with both the magnitude and slope of the data near 300 K, especially for the Mn-rich sample, suggesting that at least one other contribution to the heat capacity is present. This additional heat capacity could arise from optic phonons and/or from magnetic excitations.

V. PHYSICAL PROPERTIES OF SINGLE CRYSTALLINE Cr-, Fe- AND Sb-SUBSTITUTED BaMn_2As_2

As noted previously in Sec. II, our attempts to grow single crystals of substituted $\text{Ba}(\text{Mn}_{1-x}\text{T}_x)_2\text{As}_2$ ($T = \text{Cr, Fe, Co, Ni, Cu, Ru, Rh, Pd, Re, Pt}$) and $\text{BaMn}_2(\text{As}_{1-x}\text{Sb}_x)_2$ using Sn flux were mostly unsuccessful. The only partially successful attempts were with Cr and Fe substitutions for Mn and Sb substitution for As, where we achieved 4.4%, $\sim 10\%$ and 2.6% substitutions, respectively. These concentrations were much smaller than present in the starting compositions of the crystal growth mixtures. Here we present in-plane $\rho(T)$ and anisotropic $\chi(T)$ measurements on such Cr-, Fe- and Sb-substituted crystals, which were found to be similar to the respective properties of unsubstituted BaMn_2As_2 crystals.

A. Electrical Resistivity Measurements

The in-plane $\rho(T)$ data for single crystals of $\text{Ba}(\text{Mn}_{0.901}\text{Fe}_{0.099})_2\text{As}_2$ and $\text{Ba}(\text{Mn}_{0.956}\text{Cr}_{0.044})_2\text{As}_2$ are shown in Fig. 12. The $\rho(T)$ behaviors for both crystals exhibit monotonic increases with decreasing T below our high-temperature limit of 300 K. The resistance values below ~ 100 K became very large and exceeded the measurement limit of our instrument, indicating insulating ground states of the materials, similar to previous observations on single-crystal BaMn_2As_2 .^{14,15} An applied magnetic field of 8 T resulted in no significant change in $\rho(T)$ for either sample, as shown.

The insets of the two panels in Fig. 12 show $\ln\rho$ versus $1/T$. The data in each inset suggest two quasi-linear regions, as shown by the two straight red lines. The data in these regions follow $\ln\rho = A + \Delta/k_B T$, where A is a constant, Δ is the activation energy and k_B is Boltzmann's constant. The fitted values of the activation energies in the lowest and highest- T regions for each sample are given in the figure caption. The larger value for each sample can probably be interpreted as the intrinsic activation energy while the smaller one may be the energy gap between donor or acceptor energy levels and a conduction or valence band, respectively.³³ These observations suggest that similar to BaMn_2As_2 ,¹⁵ $\text{Ba}(\text{Mn}_{0.901}\text{Fe}_{0.099})_2\text{As}_2$ and $\text{Ba}(\text{Mn}_{0.956}\text{Cr}_{0.044})_2\text{As}_2$ are small-band-gap semiconductors.

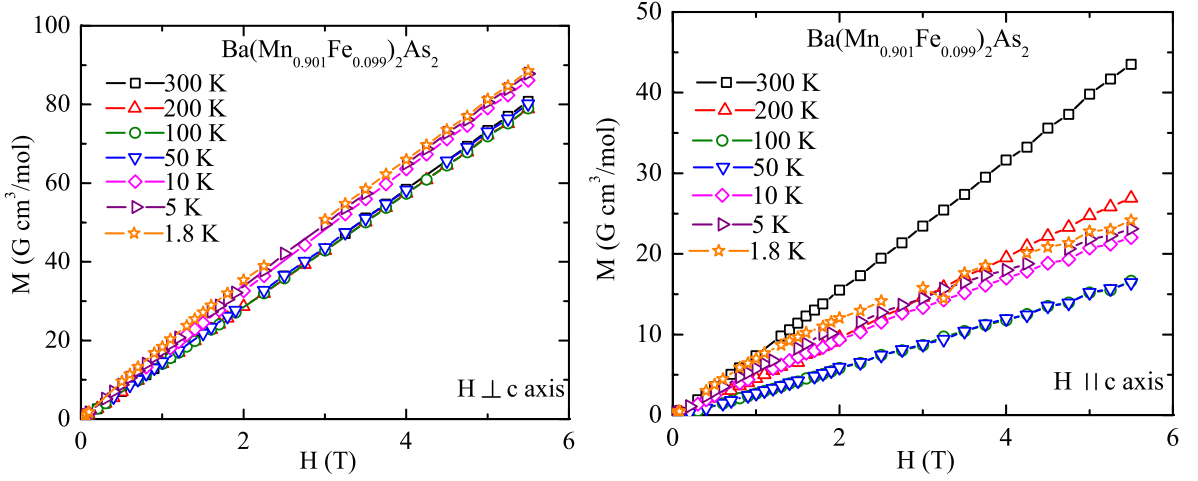


FIG. 13: (Color online) Isothermal magnetization M versus applied magnetic field H in the ab plane (top panel) and along the c axis (bottom panel) for a single crystal of $\text{Ba}(\text{Mn}_{0.901}\text{Fe}_{0.099})_2\text{As}_2$.

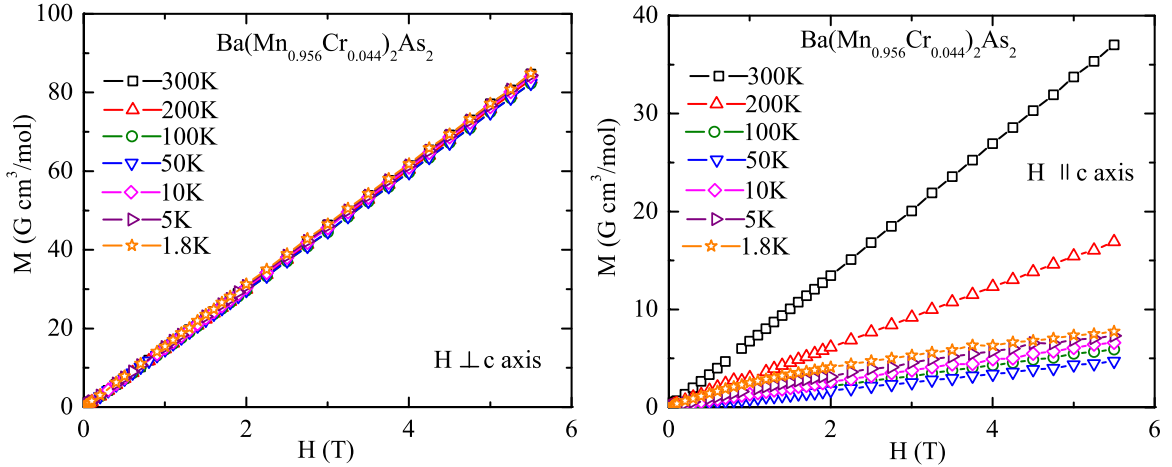


FIG. 14: (Color online) Anisotropic magnetization M versus applied magnetic field H isotherms at the indicated temperatures for $\text{Ba}(\text{Mn}_{0.956}\text{Cr}_{0.044})_2\text{As}_2$. The magnetic field was applied either in the ab plane (top panel) or along the c axis (bottom panel).

B. Magnetization and Magnetic Susceptibility Measurements

Shown in Figs. 13, 14 and 15 are $M(H)$ isotherms at temperatures from 1.8 to 300 K for single crystals of $\text{Ba}(\text{Mn}_{0.901}\text{Fe}_{0.099})_2\text{As}_2$, $\text{Ba}(\text{Mn}_{0.956}\text{Cr}_{0.044})_2\text{As}_2$ and $\text{BaMn}_2(\text{As}_{0.974}\text{Sb}_{0.026})_2$, respectively. For each compound M is proportional to H , except for temperatures $T \leq 10$ K where the data sometimes exhibit nonlinear behavior at fields below ~ 2 T. These data are similar to the above-discussed $M(H, T)$ data for quenched polycrystalline samples of $\text{Ba}(\text{Mn}_{0.8}\text{Fe}_{0.2})_2\text{As}_2$ and $\text{Ba}(\text{Mn}_{0.2}\text{Fe}_{0.8})_2\text{As}_2$, and indicate the absence of significant amounts of ferromagnetic or saturable paramagnetic impurities in the samples. In particular, the problematic relatively large amounts of ferromagnetic MnAs impurities present in BaMn_2As_2 crystals studied previously¹⁵ are not present in the present lightly substituted crystals.

Shown in Fig. 16 is the anisotropic temperature variation of the magnetic susceptibility $\chi \equiv M/H$ of the $\text{Ba}(\text{Mn}_{0.901}\text{Fe}_{0.099})_2\text{As}_2$, $\text{Ba}(\text{Mn}_{0.956}\text{Cr}_{0.044})_2\text{As}_2$ and $\text{BaMn}_2(\text{As}_{0.974}\text{Sb}_{0.026})_2$ single crystals. The susceptibilities obtained as the slopes of the high-field linear part of the $M(H)$ isotherms for temperatures ≤ 10 K, in the field range of 3–5.5 T, are also plotted as distinct symbols in Fig. 16. Similar to data for undoped BaMn_2As_2 (Ref. 15) that are also shown in the figure, the in-plane susceptibility $\chi_{ab} \sim 1.5 \times 10^{-3} \text{ cm}^3/\text{mol}$ is nearly independent of T over the whole T range of the measurement for all our crystals. In contrast, the c axis susceptibility χ_c generally decreases monotonically with decreasing T below 300 K. These observations indicate that our substituted crystals

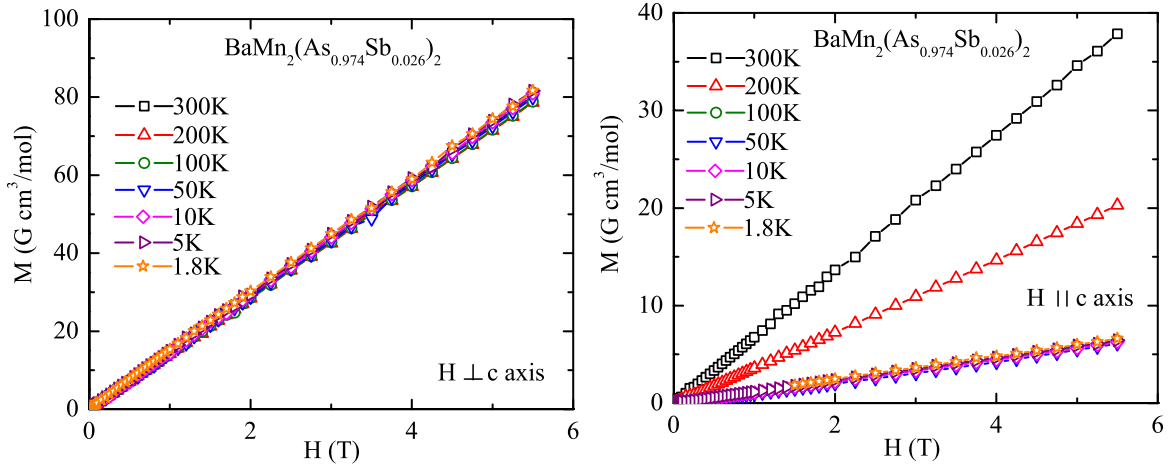


FIG. 15: (Color online) Anisotropic magnetization M versus applied magnetic field H isotherms at the indicated temperatures for $\text{BaMn}_2(\text{As}_{0.974}\text{Sb}_{0.026})_2$. The magnetic field was applied either in the ab plane (top panel) or along the c axis (bottom panel).

have magnetic properties very similar to those of unsubstituted BaMn_2As_2 and therefore that the former substituted crystals are antiferromagnetically ordered with Néel temperatures T_N far above room temperature, where $T_N = 625$ K for unsubstituted BaMn_2As_2 .¹⁶

VI. SUMMARY AND CONCLUSIONS

From our room-temperature powder XRD measurements of polycrystalline $\text{Ba}(\text{Mn}_x\text{Fe}_{1-x})_2\text{As}_2$ samples slow-cooled from 1000°C , we discovered a miscibility gap at 300 K with a composition range $0.12 \lesssim x \leq 1$. However, the miscibility gap becomes narrower at higher temperatures. For samples quenched into liquid nitrogen from 1000°C , the miscibility gap narrows to the concentration region $0.2 \lesssim x \leq 0.8$. The quenched samples of $\text{Ba}(\text{Mn}_x\text{Fe}_{1-x})_2\text{As}_2$ with $x = 0.4, 0.5$ and 0.6 contain a single 122-type phase but also contain significant amounts of impurities, mainly $\text{Fe}_{1-x}\text{Mn}_x\text{As}$ and FeAs_2 . These latter results suggest that the equilibrium phase diagram between BaMn_2As_2 and BaFe_2As_2 is not pseudo-binary in nature near the middle of the composition range.

Electrical resistivity measurements suggest that our single-phase quenched polycrystalline $\text{Ba}(\text{Mn}_{0.8}\text{Fe}_{0.2})_2\text{As}_2$ and $\text{Ba}(\text{Mn}_{0.2}\text{Fe}_{0.8})_2\text{As}_2$ samples are not metallic, but we caution that reliable resistivity data on such materials can only be obtained using single crystals. Indeed, our heat capacity measurements on these two samples reveal significant linear terms at low temperatures, suggesting metallic ground states. Our $M(H)$ measurements show that the quenched samples of $\text{Ba}(\text{Mn}_{0.8}\text{Fe}_{0.2})_2\text{As}_2$ and $\text{Ba}(\text{Mn}_{0.2}\text{Fe}_{0.8})_2\text{As}_2$ do not contain ferromagnetic impurities. The magnitudes and temperature dependences of χ around room temperature for these compositions are qualitatively consistent with those reported for BaMn_2As_2 and BaFe_2As_2 . The resistivity data, but not the susceptibility data, for $\text{Ba}(\text{Mn}_{0.8}\text{Fe}_{0.2})_2\text{As}_2$ suggest that some sort of phase transition may take place at about 260 K. Furthermore, heat capacity data for both $\text{Ba}(\text{Mn}_{0.8}\text{Fe}_{0.2})_2\text{As}_2$ and $\text{Ba}(\text{Mn}_{0.2}\text{Fe}_{0.8})_2\text{As}_2$ show no evidence for any phase transitions from 2 K to 280 K. These $C_p(T)$ data suggest that optical phonon excitations and/or magnetic excitations become important near and above room temperature.

Since the $\chi(T)$, $\rho(T)$ and $C_p(T)$ data for $\text{Ba}(\text{Mn}_{0.2}\text{Fe}_{0.8})_2\text{As}_2$ do not show any anomalies below 300 K, these data suggest that the substitution of 20% of the Fe by Mn in BaFe_2As_2 suppresses the tetragonal-to-orthorhombic and SDW transitions which are observed in BaFe_2As_2 . However, the recent work of Kim et al. found that 17.6% substitution of Fe by Mn suppresses the crystallographic transition, but not the SDW transition which still occurs at $T_N \lesssim 200$ K.¹² Furthermore, this study reported inflection points in the temperature dependences of the resistivities of their single crystal samples with $0 \leq x \leq 0.176$ that occurred at the respective composition-dependent temperatures of the structural/magnetic transition. Our resistivity measurement on polycrystalline $\text{Ba}(\text{Mn}_{0.2}\text{Fe}_{0.8})_2\text{As}_2$ in Fig. 7(b) did not show any evidence for such an inflection point. It is not clear why our measurements on polycrystalline $\text{Ba}(\text{Mn}_{0.2}\text{Fe}_{0.8})_2\text{As}_2$ do not show behaviors similar to those reported for single crystals at similar compositions.

We attempted to grow single crystals of substituted BaMn_2As_2 out of Sn flux. However, substitution of Mn by Co, Ni, Cu, Ru, Rh, Pd, Re and Pt did not occur in concentrations greater than 0.5% except for 4.4% and $\sim 10\%$ substitutions in the case of Cr and Fe, respectively, and 2.6% substitution of As by Sb. The magnetic properties of

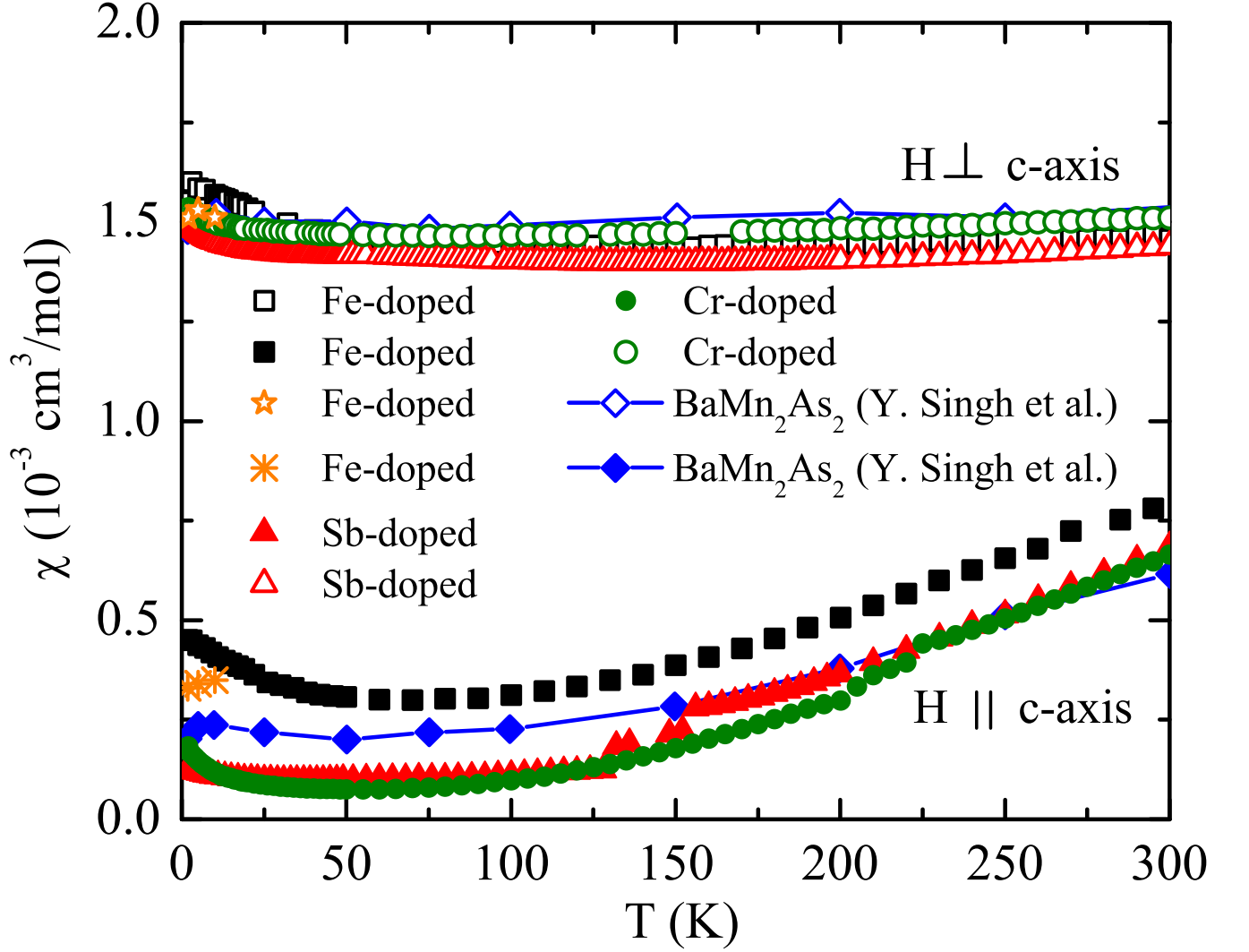


FIG. 16: (Color online) Magnetic susceptibilities χ_{ab} and χ_c in the ab plane and along the c axis, respectively, of single crystals of $\text{Ba}(\text{Mn}_{0.901}\text{Fe}_{0.099})_2\text{As}_2$, $\text{Ba}(\text{Mn}_{0.956}\text{Cr}_{0.044})_2\text{As}_2$ and $\text{BaMn}_2(\text{As}_{0.974}\text{Sb}_{0.026})_2$ versus temperature in an applied magnetic field with magnitude $H = 2-3$ T. Stars and asterisks represent the low temperature ($T \leq 10$ K) values of χ_{ab} and χ_c , respectively, extracted from $M(H)$ isotherms. For the Sb-doped and Cr-doped crystals, the spurious noise and discontinuities in the magnitude and slope of the data for $H||c$ at about 140 K and 230 K, respectively, are due to a defect in the Quantum Design SQUID magnetometer magnetic moment evaluation software that occurs when the magnetic moment of the sample plus sample holder passes through zero (here the sample holder is diamagnetic and has been corrected for in the figure). The anisotropic $\chi(T)$ data for a single crystal of BaMn_2As_2 obtained by Singh et al. (Ref. 15) are included for comparison.

Fe-, Cr- and Sb-substituted BaMn_2As_2 crystals are similar to those of pure BaMn_2As_2 .

Acknowledgments

We are grateful to Yogesh Singh and Andreas Kreyssig for helpful discussions, Supriyo Das for assistance with laboratory activities, and Makariy Tanatar for advice on making electrical contacts to the samples for resistivity measurements. Work at the Ames Laboratory was supported by the Department of Energy-Basic Energy Sciences

under Contract No. DE-AC02-07CH11358.

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