Magnetism in La$_2$O$_3$(Fe$_{1-x}$Mn$_x$)$_2$Se$_2$ tuned by Fe/Mn ratio

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(Dated: May 3, 2014)

We report the evolution of structural and magnetic properties in La$_2$O$_3$(Fe$_{1-x}$Mn$_x$)$_2$Se$_2$. Heat capacity and bulk magnetization indicate increased ferromagnetic component of the long range magnetic order and possible increased degree of frustration. Atomic disorder on Fe(Mn) sites suppresses the temperature of the long range order whereas intermediate alloys show rich magnetic phase diagram.

PACS numbers: 74.25.Wx, 74.25.F-, 74.25.Op, 74.70.Dd

I. INTRODUCTION

Parent materials of cuprates and iron-based superconductors are layered transition-metal compounds (TMP’s) with antiferromagnetic (AFM) ground state due to a dissimilar magnetic mechanism and with rather different electronic conductivity. Local environment of TM is intimately connected with this since puckering of iron pnictide crystallographic layers promotes higher conductivity in parent materials of iron superconductors, as opposed to cuprates. Recently, a family of layered TMP oxychalcogenides Ln$_2$O$_3$TM$_2$Ch$_2$ (Ln = rare earth, TM = transition metal, and Ch = S, Se) and its analogues A$_2$F$_2$TM$_2$OCh$_2$ (A = Sr, Ba) has received more attention. They have anti-CuO$_2$-type TM$_2$OCh$_2$ layers and the local environment of TM bears much more resemblance to manganites or cuprates than to iron based superconductors. This typically results in semiconducting or Mott insulating ground state with AFM transition. Within the TM$_2$OCh$_2$ layers transition metal atoms are located at the distorted octahedral environment due to the different distances of TM-Ch and TM-O, whereas the TM-Ch(O) octahedrons are face sharing. This distortion lifts the degeneracy of $e_g$ and $t_{2g}$ levels in a non-distorted octahedral crystal field. The TM$_2$OCh$_2$ layers in the crystal structure harbor three principal competing interactions: the nearest neighbor (NN) $J_3$ interaction of the closest TM atoms in the crystallographic ab plane, next nearest neighbor (NNN) superexchange interaction $J_2$ of nearly 90° TM-Ch-TM, and (NNN) $J_1$ superexchange interaction of 180° TM-O-TM. Theoretical calculation and neutron diffraction results indicate that the AFM transition stems from the competition of three interactions in an unusual frustrated AFM checkerboard spin-lattice system. Frustrated magnetic order on checkerboard lattices hosts rich magnetic ground states and could be relevant to physics of colossal magnetoresistance manganites and iron based and cuprates superconducting materials. Therefore it is of interest to address the nature of magnetic order and frustration in 2322 materials since it shares some characteristics of all the above mentioned compounds.

Among 2322 materials, La$_2$O$_3$Mn$_2$Se$_2$ exhibits a faint specific heat anomaly at AFM transition and two dimensional (2D) short range magnetic correlations that lock magnetic entropy far above the temperature of the bulk long range AFM transition. Weak ferromagnetic (FM) component superimposed on the paramagnetic background in M(H) loops at 2 K proposed to arise due to spin reorientation and/or spin canting below the AFM transition might also come from magnetic impurities such as Mn$_3$O$_4$. Mn-2322 has a G-type AFM structure with the ordered moment along the c axis direction and where NN Mn ions have opposite spins with dominant AFM $J_3 < 0$ and fully frustrated $|J_1| < J_2$ with $J_1 < 0$ and $J_2 > 0$. On the other hand, La$_2$O$_3$Fe$_2$Se$_2$ adopts magnetic structure similar to FeTe where half of the $J_3$, $J_2$ and $J_1$ are frustrated and different from the theoretical predictions. This is different from other compounds with same structure, in which $J_1$ is the dominant term.

In this work we tuned the magnetism on Fe/Mn checkerboard lattice by varying TM content and examined the magnetic ground states of La$_2$O$_3$(Fe$_{1-x}$Mn$_x$)$_2$Se$_2$ series. We find that Mn substitution lead to the increase of activation energies for the electrical transport energy gap $E_a$ and has strong effect on magnetic phase diagram and the spin entropy release above the temperature of the long range magnetic order.

II. EXPERIMENT

La$_2$O$_3$(Fe,Mn)$_2$Se$_2$ polycrystals were synthesized by solid state reaction from high purity materials (≥ 99%). Dried La$_2$O$_3$ powder, Mn lump, Fe and Se powders were mixed and ground in an agate mortar. The mixture was pressed into pellets and sealed in a quartz tube backfilled with pure Argon gas. The ampule was heated to 1273 K and reacted for 24 h followed by furnace cooling. This was repeated several times to en-
sure homogeneity. The color of final product is yellowish green for Mn-2322 and black for Fe-2322.

Powder X-ray diffraction (XRD) patterns of the ground samples were taken with Cu $K_\alpha = 0.1458$ nm using a Rigaku Miniflex X-ray machine. The structural parameters were obtained by Rietveld refinement using Rietica software. Single crystal X-ray data were collected in a Bruker Kappa Apex II single crystal X-ray diffractometer at the room temperature with Mo $K_\alpha = 0.071073$ nm on a 20 $\mu$m single crystal isolated from the polycrystalline powder. Single crystal unit cell refinement was performed with Bruker APEX 2 software package. Time-of-flight neutron diffraction measurements were carried out at 300 K on the high intensity powder diffractometer (HIPD) of the Lujan Neutron Scattering Center at the Los Alamos National Laboratory. Pulverized samples were loaded in extruded vanadium containers in helium atmosphere and sealed. Data were collected for 1 hour for each sample. Rietveld refinements of the data were carried out using GSAS software within the I4/mmm space group.

Mössbauer spectra were taken in transmission mode with $^{57}$Co(Rh) source at 294 K and the parameters were obtained using WinNormos software. Calibration of the spectrum was performed by laser and isomer shifts were given with respect to $^{57}$Fe.

Thermal, transport and magnetic measurements were carried out in a Quantum Design PPMS-9 and MPMS-5. The samples were cut into rectangular parallelepipeds and thin Pt wires were attached for four probe resistivity measurements. Sample dimensions were measured with an optical microscope Nikon SMZ-800 with 10 $\mu$m resolution.

III. RESULTS AND DISCUSSIONS

Crystal structure of (Fe,Mn)-2322 and principle magnetic interactions $J_{1-2}$, $J_1$, $J_3$ are shown in Fig. 1(a,b). Both XRD and neutron reflections can be indexed using a tetragonal unit cell (Fig. 1(c,d)), indicating a continuous solid solution between Mn-2322 and Fe-2322. Unit cell of Mn-2322 single crystal determined from the single crystal X-ray experiment was I4/mmm with $a = 0.417(3)$ nm and $c = 1.89(2)$ nm, in agreement with the powder data. Powder X-ray and neutron lattice parameters are shown in Fig. 1(e) and details of the crystal structure extracted from the neutron data, listed in Tables I-III, are consistent with the reported values.

For Mn-2322, using obtained Mn-Se and Mn-O bond lengths (shown in Table 1), we calculate the valence of Mn ions using the bond valence sum (BVS) formalism in which each bond with a distance $d_{ij}$ contributes a valence $v_{ij} = \exp[(R_{ij} - d_{ij})/0.37]$ with $R_{ij}$ as an empirical parameter and the total of valences of atom $i$, $V_i$ equals $V_i = \sum_j v_{ij}$. The calculated valence of Mn ions is +2.03, consistent with the apparent oxidation state (+2) for Mn atoms. With increase in Mn content, the lattice parameters increase gradually for both $a$ and $c$ axes, hence the unit cell of Mn-2322 is larger than Fe-2322, which itself is larger than the unit cell of La$_2$O$_2$Co$_2$OSe$_2$ (Co-2322) [23]. This trend can be explained by the larger ionic size of Mn$^{2+}$ when compared to Fe$^{2+}$ and Co$^{2+}$ ions, giving some insight in the spin state of Mn$^{2+}$ ions. The lattice parameters should be proportional to the ionic size, $r_{TM^{2+}}$, of transition metals TM$^{2+}$ (TM = Mn, Fe, and Co). Therefore from the observation $a_{Mn} = 0.41334$ nm $> a_{Fe} = 0.40788$ nm $> a_{Co} = 0.40697$ nm and $c_{Mn} = 1.88221$ nm $> c_{Fe} = 1.86480$ nm $> c_{Co} = 1.84190$ nm we conclude that $r_{Mn^{2+}} > r_{Fe^{2+}} > r_{Co^{2+}}$. M"{o}ssbauer spectra and theoretical calculations for Fe-2322 and Co-2322 suggest that Fe$^{2+}$ and Co$^{2+}$ are in the high spin state. This is in agreement with $r_{Fe^{2+}} (0.0780$ nm) $> r_{Co^{2+}} (0.0745$ nm) for high spin (HS) state (coordination number = 6). Therefore, the Mn$^{2+}$ ions should be in the HS state since $r_{Mn^{2+}} (LS) = 0.067$ nm (LS = low spin) and $r_{Mn^{2+}} (HS) = 0.083$ nm for Mn$^{2+}$ with 6-fold coordination.

![FIG. 1. (a) Crystal structure of (Fe,Mn)-2322. (b) TM-O planes shown for TM = Fe. Se atoms (green) are puckered above and below the plane, with Se-Fe-Se angle 97.04°. (c) and (d) XRD and neutron powder diffraction results at room temperature for the Mn-2322 polycrystal, respectively. (e) Lattice parameters for (Fe,Mn)-2322 determined from neutron diffraction (stars) and XRD (circles).]
TABLE I. Structural parameters for La$_2$O$_3$Fe$_2$Se$_2$ at 300 K.

| Chemical Formula | La$_2$O$_3$Fe$_2$Se$_2$ |
|------------------|-------------------------|
| Interatomic Distances (nm) | Bond Angles (°) |
| $d_{Fe-O}$ | 0.20413(1) | O-Fe-O 180 |
| $d_{Fe-Se}$ | 0.27129(8) | Se-Fe-Se 97.61(4)/82.39(4) |
| $d_{Fe-Fe}$ | 0.28869(1) | Se-Fe-O 90 |
| Atom | x | y | z | Occ | $U_{iso}$ (10$^{-2}$nm$^2$) |
| La | 0.5 | 0.5 | 0.1843(1) | 1 | 0.0026(2) |
| O1 | 0.5 | 0 | 0.25 | 1 | 0.0059(3) |
| O2 | 0.5 | 0 | 0 | 1 | 0.0124(5) |
| Fe | 0 | 0 | 0 | 1 | 0.0059(2) |
| Se | 0 | 0 | 0.0962(1) | 1 | 0.0032(2) |

TABLE II. Structural parameters for La$_2$O$_3$(Fe$_{0.5}$Mn$_{0.5}$)$_2$Se$_2$ at 300 K.

| Chemical Formula | La$_2$O$_3$(Fe$_{0.5}$Mn$_{0.5}$)$_2$Se$_2$ |
|------------------|-------------------------|
| Interatomic Distances (nm) | Bond Angles (°) |
| $d_{Fe/Mn-O}$ | 0.20528(1) | O-Fe-O 180 |
| $d_{Fe/Mn-Se}$ | 0.27641(12) | Se-Fe-Se 95.92(6)/84.08(6) |
| $d_{Fe/Mn-Fe/Mn}$ | 0.29031(1) | Se-Fe/Mn-O 90 |
| Atom | x | y | z | Occ | $U_{iso}$ (10$^{-2}$nm$^2$) |
| La | 0.5 | 0.5 | 0.1851(1) | 1 | 0.0057(3) |
| O1 | 0.5 | 0 | 0.25 | 1 | 0.0051(5) |
| O2 | 0.5 | 0 | 0 | 1 | 0.0100(7) |
| Fe | 0 | 0 | 0 | 1 | 0.0058(8) |
| Se | 0 | 0 | 0.0987(1) | 1 | 0.0044(4) |

TABLE III. Structural parameters for La$_2$O$_3$Mn$_2$Se$_2$ at 300 K.

| Chemical Formula | La$_2$O$_3$Mn$_2$Se$_2$ |
|------------------|-------------------------|
| Interatomic Distances (nm) | Bond Angles (°) |
| $d_{Mn-O}$ | 0.2667(1) | O-Mn-O 180 |
| $d_{Mn-Se}$ | 0.28030(1) | Se-Mn-Se 95.01(1)/84.99(1) |
| $d_{Mn-Mn}$ | 0.29227(1) | Se-Fe/Mn-O 90 |
| Atom | x | y | z | Occ | $U_{iso}$ (10$^{-2}$nm$^2$) |
| La | 0.5 | 0.5 | 0.1866(2) | 1 | 0.0042(5) |
| O1 | 0.5 | 0 | 0.25 | 1 | 0.0057(7) |
| O2 | 0.5 | 0 | 0 | 1 | 0.0015(8) |
| Mn | 0.5 | 0 | 0 | 1 | 0.0086(8) |
| Se | 0 | 0 | 0.1006(1) | 1 | 0.0020(5) |

TABLE IV. Mössbauer isomer shifts $\delta$ and electric field quadrupole splittings $\Delta E_Q$ for La$_2$O$_3$(Fe$_{1-x}$Mn$_x$)$_2$Se$_2$ at 294 K.

| Chemical formula | $\delta$(mm/s) | $\Delta E_Q$(mm/s) | $\Gamma$(mm/s) |
|------------------|----------------|----------------|---------------|
| La$_2$O$_3$Fe$_2$Se$_2$ | 0.895(1) | 1.952(1) | 0.287(2) |
| La$_2$O$_3$(Fe$_{0.8}$Mn$_{0.2}$)$_2$Se$_2$ | 0.90(4) | 1.756 | 0.309 |
| La$_2$O$_3$(Fe$_{0.5}$Mn$_{0.5}$)$_2$Se$_2$ | 0.812(6) | 1.60(1) | 0.309(7) |

FIG. 2. Mössbauer spectra of La$_2$O$_3$(Fe$_{1-x}$Mn$_x$)$_2$Se$_2$ for $x = 0$ (a), $x = 0.2$ (b), and $x = 0.5$ (c), respectively. Vertical arrows denote relative positions of peaks with respect to the background. The data were shown by open circles and the fit is given by the red solid line. The doublets of the main (blue) and impurity (green) phases are offset for clarity. Inset shows the distributions of the electrical quadrupole splitting at the $^{57}$Fe spectrum of La$_2$O$_3$(Fe$_{0.8}$Mn$_{0.2}$)$_2$Se$_2$.

Mössbauer isomer shifts $\delta$ are sensitive on the electron density on a nucleus. Electric quadrupole splitting $\Delta$ arises due to interaction between electric field gradient and nuclear quadrupole moment. The $\delta$ and $\Delta$ provide information of the oxidation, spin state, chemical bonding and site symmetry. Mössbauer spectra of Fe-2322 (Fig. 2(a)) shows a single doublet, consistent with a single inequivalent 4c position of Fe in I4/mmm space group of the unit cell. Isomer shifts $\delta = 0.895(1)$ mm/s and quadrupole splitting ($\Delta = 1.952(1)$ mm/s) are well in agreement with the high spin $S = 2$ of Fe$^{2+}$ in the D$_{2h}$ symmetry site of FeO$_2$Se$_2$ octahedra. However, the $\Delta = 0.29031(1)$ mm/s discrepancy between the experimental and theoretical fits and the mild asymmetry of peak intensities suggest that another interaction is superimposed on the main doublet. The Fe$^{2+}$ experiences either an additional doublet or sextet due to an impurity phase or a high temperature magnetism in the sample with magnetic dipole interaction of $\mu_H \ll eV_{zz}Q$ magnitude. However, no known impurity phase, including LaFeO$_3$ was able to explain the experimental spectra. In contrast, Mössbauer spectra in both La$_2$O$_3$(Fe$_{0.5}$Mn$_{0.5}$)$_2$Se$_2$...
and La₂O₃(Fe₀.8Mn₀.2)₂Se₂ detected Fe-Se phase impurity with δ = 0.45(7) mm/s, Δ = 0.8(1) mm/s. When Mn substitutes Fe in 1:4 ratio (Fig. 2(b)) there are 8 Fe²⁺ ions in the first two coordination spheres which contribute to 10 different combinations after the substitution if all combinations are of equal probability. The most important contribution to hyperfine interactions is from the first coordination sphere. With 1:4 Mn to Fe ratio there are 3 different combinations: with 0, 1 or 2 Mn on four Fe sites. The ratio of these combinations is 17:20:3 respectively. Distribution of electric quadrupole splittings centered at 1.756 mm/s, with 0.309 mm/s standard deviation and pronounced tail near the smaller values confirms uniform distribution of Mn. The main doublet and minority phase (or interaction) are also present when one half of Fe²⁺ is replaced by Mn²⁺ in La₂O₃(Fe₀.5Mn₀.5)₂Se₂ (Fig. 2(c)). The atomic positions where half of Fe ions were substituted by Mn are symmetric within the first coordination sphere around Fe²⁺ that contains FeO₂Se₂ and four closest Fe ions in the Fe-O planes (Fig. 1(a)). This is confirmed by the rather small widening of the doublet lines (Γ = 0.309 (7) mm/s). Decreased values of isomer shift δ suggest a change in the charge density on the Fe²⁺ and substantial decrease of the octahedra.

In order to complement the Mössbauer measurements, we performed density functional theory (DFT) calculations using the WIEN2K all-electron full-potential APW+lo code. For La, Fe, Mn, Se, and O atoms the muffin-tin sphere radii were set to 2.38, 1.86, 1.86, 2.5 and 1.62 a.u.. The basis set functions were expanded up to R_mₖₖₖₖₖₖ = 7. We used the LDA-Fock-0.25 hybrid functional, which provides a viable alternative to the LDA+U approach in describing the electron correlations in this system. Starting from the Fe-2322 and Mn-2322 pure structures, we constructed 2×2×1 supercells of La₂O₃(Fe₀.25Mn₀.75)₂Se₂, La₂O₃(Fe₀.5Mn₀.5)₂Se₂ and La₂O₃(Fe₀.75Mn₀.25)₂Se₂ to approximate the mixed Fe-Mn systems. Figure 3 shows the total density of states (DOS) as calculated for the FM state of the investigated compounds.

The LDA-Fock-0.25 hybrid functional calculations correctly predict the Mott-insulating behavior of (Fe, Mn)-2322. The band gaps are similar but decrease somewhat from pure Fe-2322 (about 0.4 eV) to pure Mn-2322 (about 0.25 eV). The overall shape of the DOS across this group is very similar, one significant distinction being the band gap shift of the minority DOS towards lower energies with increased Mn content. In our checkerboard AFM LDA-Fock-0.25 calculations (carried out only for the end compounds, not shown here), the band gaps of Fe-2322 and Mn-2322 are found to be 1.85 and 0.99 eV, respectively. Our calculations indicate that the AFM state is more stable than the FM state by 0.75 eV in Fe-2322 and 0.43 eV in Mn-2322. The supercell approach also enabled us to calculate the electric field gradient (EFG) and isomer shift (IS) at Fe situated in several different local coordinations. In Figure 4 we com-

FIG. 3. Total DOS per formula unit for the FM state of (Fe, Mn)-2322. The Fermi level is set to zero energy. There is a band gap shift of the minority DOS towards lower energies as Mn substitutes Fe in the lattice.
pare the results of our calculations with the values extracted from Mössbauer spectroscopy. While our calculations were able to reproduce the values of the measured EFGs, the ISs are found to be smaller than the experimental values by up to 20 percent. The discrepancy is because experimental Mössbauer includes second order Doppler shift and chemical isomer shift due to electronic density whereas the theoretical parts involves only the latter. The calculated EFG of $11.6 \times 10^{21} \text{V/m}^2$ in pure Fe-2322 agrees very well with the EFG obtained in similar DFT calculations.

Neglecting grain boundaries, Mn-2322 resistivity at room temperature is about $2 \times 10^4 \, \Omega \cdot \text{cm}$. This is two orders of magnitude smaller than Co-2322.

The resistivities of (Fe,Mn)-2322 exhibit activated behavior, $\rho = \rho_0 \exp\left(\frac{E_a}{k_B T}\right)$, where $\rho_0$ is the prefactor, $E_a$ is the activation energy, $k_B$ is the Boltzmann’s constant and $T$ is temperature (Fig. 5(a) and (b)). By fitting the $\rho(T)$ data from 210 to 320 K we obtain the activation energy $E_a = 0.2425(2)$ eV for Mn-2322. This is substantially smaller than the activation energy of Co-2322 and consistent with the recently reported value. The $E_a$ decreases rapidly by $x = 0.5$ (0.1814(3) eV), then gradually as the Mn/Fe ratio is tuned to Fe-2322 (0.1796(3) eV).

The value of $E_a$ for Fe-2322 is close to that reported in the literature. The residual resistivity values ($\rho_0$) exhibit the same trend. These results indicate that the band gap of (Fe,Mn)-2322 decreases with the contraction of lattice parameters. The narrowing of band gap is also consistent with sample color changes from yellowish green in Mn-2322 to black in Fe-2322. Gap values obtained for Mn-2322 are in agreement with LDA calculations (Fig. 3), however for Fe-2322 and for intermediate alloys there is a disagreement. This suggests increased importance of strong electronic correlations for increased Fe site occupancy of Fe/Mn site in (Fe, Mn)-2322 alloys.

Temperature dependence of dc magnetic susceptibility $\chi(T) = M/H$ taken in 50 kOe magnetic field for (Fe,Mn)-2322 with zero field cooling (ZFC) is shown in Fig. 6(a). For Fe-2322, there is AFM transition at $T_N = 90$ K, consistent with previous results. With Mn doping, this AFM transition shifts to lower temperature quickly and disappears in Mn-2322. On the other hand, there is other FM-like transition emerging and shifting to higher temperature when Mn enters the lattice. Finally, for Mn-2322, The $\chi(T)$ curves of Mn-2322 (inset of Fig. 6(a)) exhibit three features: one broader maximum, $T_{Max}$ and two anomalies, $T_{M1}$ and $T_{M2}$. $T_{Max}$ (~ 275 K) with no Curie-Weiss behavior up to 350 K implies that there is a stronger two-dimensional short-range spin correlations in Mn-2322 than in Fe-2322 at high temperature, reflecting the frustrated nature of the magnetic structure in Mn-2322. From the sharp minimum of the $d(\chi(T))/dT$ curves (Fig. 6(b)) we extract $T_{M1} \sim 164$ K, in agreement with previous results. The $T_{M1}$ anomaly is field independent and therefore should have considerable ferromagnetic component due to canting and/or magnetocrystalline anisotropy possibly induced by frustration. The second anomaly (minimum in $d(\chi(T))/dT$ at $T_{M2} = 122$
FIG. 6. (a) Temperature dependence of the magnetic susceptibility \( \chi(T) \) for (Fe,Mn)-2322 taken in 50 kOe. Inset shows enlarged \( \chi(T) \) for Mn-2322. (b) \( d(\chi(T))/dT \) of Mn-2322 at various magnetic fields for ZFC magnetization. (c) ZFC and FC curves of Mn-2322 near magnetic transitions.

K (inset of Fig. 6(a))) is also field independent, however it is strongly suppressed in high fields. This is in agreement with its proposed spin reorientation origin.\(^{[13]}\) The ZFC and field cooling (FC) \( \chi(T) \) curves split at \( T_{c2} \) but gradually overlap with magnetic field increase (Fig. 6(c)). This implies the presence of either magnetic frustration or magnetocystalline anisotropy. On the other hand, \( \chi(T) \) of Mn-2322 show a hump around \( T_N = 42 \) K at 1 kOe with ZFC mode (blue curve), similar to previous results.\(^{[13][14]}\) It could be due to superparamagnetic Mn\(_3\)O\(_4\) nanoparticles contamination below our diffraction resolution limit.\(^{[13]}\) Overall, the substantial shift of the cusp with \( x \) and evolution of FM-like increase of magnetization above the cusp temperature points to development of intrinsic magnetic interactions from Fe-2322 to Mn-2322. With Mn doping, the part of magnetic entropy that contributes to long range order rapidly shifts to lower temperature whereas frustration-induced FM (or canting, anisotropic exchange interactions) component of magnetization increases and high temperature two-dimensional short range magnetic order becomes stronger as the magnetic system is tuned toward the lattice with full Mn occupation.

Specific heat of (Fe,Mn)-2322 (Fig. 7) approaches the value of 3NR at 300 K, where \( N \) is the atomic number in the chemical formula (\( N = 9 \)) and \( R \) is the gas constant (\( R = 8.314 \) J mol\(^{-1}\) K\(^{-1}\)), consistent with the Dulong-Petit law. On the other hand, Fe-2322 specific heat shows a \( \lambda \)-type anomaly at \( T = 89 \) K for Fe-2322 in agreement with the result in the literature.\(^{[11]}\) This anomaly is due to a long-range 3D antiferromagnetic (AFM) ordering of the Fe\(^{2+}\). After subtraction of the phonon contribution (\( C_{ph} \)) fitted using a polynomial for the total specific heat, we obtain the magnetic contribution (\( C_{mag} \)) and calculate the magnetic entropy using \( S_{mag}(T) = \int_0^T C_{mag}/T \) dT. The derived \( S_{mag} \) is 3.23 J/mol-K at 120 K, which is much smaller than the expected value (\( \sim 24\% \) Rln(2S + 1) = Rln5) for Fe\(^{2+}\) ions with high spin state (inset of Fig. 7). Note that only about half of that value is released below \( T_N \). It suggests that substantial fraction of magnetic entropy is locked at high temperatures due to possible 2D short-range magnetic order before long range correlations develop at \( T_N \).\(^{[11]}\) In contrast, there is no \( \lambda \)-type anomaly for Mn-2322 at the temperature of magnetic transitions.
both raise rapidly as Mn enters the lattice. In (Fe,Mn)-2322 compounds long range magnetic order competes with disorder induced by geometric spin frustration. Atomic disorder on Fe/Mn sites tips this balance and promotes frustration. Since the balance of all 3 principle interactions $J_1-J_3$ can be tuned by Fe/Mn ratio, this system might be mapped to the 2D pyrochlore where charge order and metal to insulator transition have been predicted at half filling.\cite{13}

V. ACKNOWLEDGEMENTS

The part of this work was carried out at BNL which is operated for the U.S. Department of Energy by Brookcases Science Associates under grant DE-AC02-98CH10886. A portion of this work was benefited from the use of HIPD at the Lujan Center at Los Alamos Neutron Science Center, funded by DOE Office of Basic Energy Sciences. Los Alamos National Laboratory is operated by Los Alamo National Security LLC under DOE Contract No. DE-AC52-06NA25396. This work has also been supported by the grant No. 45018 from the Serbian Ministry of Education and Science.

1. I. I. Mazin, Nature 464, 183 (2010).
2. V. Cvetkovic and Z. Tesanovic, Europhys. Lett 85, 37002 (2009).
3. M. M. Qazilbash, J. J. Hamlin, R. E. Baumbach, L. Zhang, D. J. Singh, M. B. Maple and D. N. Basov, Nature Phys. 5, 647 (2009).
4. J. M. Mayer, L. F. Schneemeyer, T. Siegrist, J. V. Waszczak and B. Van Dover, Angew. Chem., Int. Ed. Engl. 31, 1645 (1992).
5. S. J. Clarke, P. Adamson, S. J. C. Herkelrath, O. J. Rutt, D. R. Parker, M. J. Pitcher and C. F. Smura, Inorg. Chem. 47, 8473 (2008).
6. H. Kabbour, E. Janod, B. Corraze, M. Danot, C. Lee, M. H. Whangbo and L. Cario, J. Am. Chem. Soc. 130, 8261 (2008).
7. C. Wang, M. Q. Tan, C. M. Feng, Z. F. Ma, S. Jiang, Z. A. Xu, G. H. Cao, K. Matsubayashi and Y. Uwatoko, J. Am. Chem. Soc. 132, 7069 (2010).
8. J. X. Zhu, R. Yu, H. Wang, L. L. Zhao, M. D. Jones, J. Dai, E. Abrahams, E. Morosan, M. Fang and Q. Si, Phys. Rev. Lett. 104, 216405 (2010).
9. D. G. Free and J. S. O. Evans, Phys. Rev. B 81, 214433 (2010).
10. H. Wu, Phys. Rev. B 82, 020410 (2010).
11. Y. Fuwa, M. Wakeshima and Y. Hinatsu, J. Phys. Cond. Matt. 22, 346003 (2010).
12. Y. Fuwa, T. Endo, M. Wakeshima, Y. Hinatsu and K. Ohoyama, J. Am. Chem. Soc. 132, 18020 (2010).
13. E. E. McCabe, D. G. Free, B. G. Mendis, J. S. Higgins and J. S. O. Evans, Chem. Mater. 22, 6171 (2010).
14. N. Ni, E. Climent-Pascual, S. Jia, Q. Huang and R. J. Cava, Phys. Rev. B 82, 214419 (2010).
15. R. H. Liu, J. S. Zhang, P. Cheng, X. G. Luo, J. J. Ying, Y. J. Yan, M. Zhang, A. F. Wang, Z. J. Xiang, G. J. Ye and X. H. Chen, Phys. Rev. B 83, 174450 (2011).
16. D. G. Free, N. D. Withers, P. J. Hickey and J. O. Evans, Chem. Mater. 23, 1625 (2011).
17. C. D. Ling, J. E. Millburn, J. F. Mitchell, D. N. Argyriou, J. Linton and H. N. Bordallo, Phys. Rev. B 62, 15906 (2000).
18. U. Löw, V. J. Emery, K. Fabricius and S. A. Kivelson, Phys. Rev. Lett. 72, 1918 (1994).
19. T. Yildirim, Phys. Rev. Lett. 101, 057010 (2008).
20. Q. Si and E. Abrahams, Phys. Rev. Lett. 101, 076401 (2008).
21. M. J. Han, Q. Yin, W. S. Pickett and S. Y. Savrasov, Phys. Rev. Lett. 102, 107003 (2009).
22. S. Li, C de la Cruz, Q. Huang, Y. Chen, J. W. Lynn, J. Hu, Y. L. Huang, F. C. Hsu, K. W. Yeh, M. K. Wu and P. C. Dai, Phys. Rev. B 79, 054503 (2009).
23. B. Hunter, Int. Un. of Cryst. Comm. Newsletter 20 (1998).
24. A. C. Larson, and R. B. Von Dreele, General structure analysis system, Report No. LAUR-86-748, Los Alamos National Laboratory, Los Alamos, NM, (2000).
25. B. H. Toby, J. Appl. Crystallogr. 34, 201 (2001).
26. R. A. Brand, WinNormos Mössbauer fitting program, Universität Duisburg 2008
27. I. D. Brown and D. Altermatt, Acta Crystalogr. Sect. B 41, 244 (1985).
28. N. E. Brese and M. O’Keefe, Acta Crystalogr. Sect. B 47, 192 (1991).
29. P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka, and J. Luitz, "WIEN2k, an augmented plane wave + local orbitals program for calculating crystal properties.”, (Karlheinz Schwarz, Techn. Universität Wien, Austria), 2001. ISBN
30. F. Tran, P. Blaha, K. Schwarz, and P. Novák, Phys. Rev. B \textbf{74}, 155108 (2006).

31. F. Yayoi, W. Makoto, and H. Yukio, J. Phys.: Condens. Matter \textbf{22}, 346003 (2010).

32. S. Fujimoto, Phys. Rev. Lett. \textbf{89}, 226402 (2002).

33. S. Fujimoto, Phys. Rev. B \textbf{67}, 235102 (2003).