Mechanism of Isostructural Phase Transition in Fe-Mn Solid Solutions

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Abstract

Experimental measurements indicate that the body-centered cubic solid solution undergoes a phase transition at approximately 2.0 at.% Mn, but the mechanism of this phase transition and the changes in physical properties of the Fe-Mn system before and after the transition remain unclear to date. This study employs density functional theory calculations to reveal that this phase transition is an isostructural phase transition, and elucidates the phase transition mechanism and the changes in physical properties before and after the transition.

Full Text

Preamble

Electronic Mechanisms on the Iso-Structural Phase Transition in Fe-Mn Solid Solution

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Abstract

Experiments have consistently shown that dilute solid solutions of manganese in body-centered cubic iron transform from antiferromagnetic to ferromagnetic coupling at approximately 2 at.% Mn. Despite extensive theoretical investigation, this phase transition remains poorly understood, and its underlying mechanism is still unresolved. Based on density functional theory (DFT) calculations employing dense k-point meshes, we reveal that this "iso-structural" phase transition (IPT) occurs at 1.85 at.% Mn, originating from the shifting of the Mn 3d e__g level across the Fermi level and the consequent intra-atomic electron transfer within the Mn 3d states. The IPT involves a sudden change in bulk modulus accompanied by a small yet detectable change in lattice constant, an inversion of magnetic coupling between solute Mn and the Fe matrix, and a change in bonding strength between Mn and its first-nearest-neighbor Fe atoms. Our interpretation of this IPT provides enlightening insights for understanding similar IPTs in other materials.

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In condensed matter physics, iso-structural phase transitions are particularly remarkable due to their unusual nature. For example, cerium transforms from the γ to α phase at approximately 8 kBar and ambient temperature, accompanied by a volume collapse of ~17% and an electric resistance drop of ~40% [?]. Experiments have shown that IPTs in some materials are associated with intriguing phenomena such as negative thermal expansion, giant magneto-elastic coupling, and large piezoelectric response, indicating potential technological applications [?]. Great efforts have been made to study IPT mechanisms for over half a century. Some studies have focused on the role of phonon dynamics [?, ?], while others have emphasized electronic origins. It was found that electronic valence transitions in rare-earth elements lead to IPTs in YbGaGe [?], $YbInCu_4$ [?], Eu(Pd_1 Au)$_2Si_2$ [?], and SmS [?]. However, the electronic origin of other prototypical IPTs, including the $\gamma\rightarrow\alpha$ Ce transition and the insulator→metal transition of V_2O_3, remains incompletely understood [?]. This is because experimental measurements are inconsistent with the valence transition model and cannot provide detailed information to interpret the electronic processes during these IPTs [?, ?]. From a theoretical perspective, a reasonable description of these IPTs requires accurate treatment of correlation effects by considering the many-body N-electron configuration [?], which is beyond standard density functional theory. The electronic density of states (DOS) of Ce in either phase calculated by DFT does not reproduce the famous three-peak structure of experimental spectra [?, ?]. The mechanism of the V_2O_3 insulator→metal transition has remained under debate [?, ?]. Furthermore, current DFT methods, as well as hybrid approaches combining DFT with other techniques, cannot produce two distinct solutions (phases) for these materials and capture transitions between them within a single computational framework.

On the other hand, experiments suggest a phase transition occurs in body-centered cubic (bcc) Fe-Mn alloys with increasing Mn concentration. Neutron diffraction measurements yield Mn values of -0.82, 0, and 0.6 B at 0.79, 1.5, and 2.0 at.% Mn, respectively, at room temperature [?]. At 2.0 at.% Mn and higher concentrations, all experiments report positive Mn values [?, ?, ?]. Long-term efforts have been devoted to theoretically studying the variation of Mn with Mn concentration in bcc Fe-Mn alloys. Linear-muffin-tin-orbital (LMTO) Green' s function calculations showed that both ferromagnetic (FM, Mn>0) and antiferromagnetic (AFM, Mn<0) coupling states of Mn with the bcc Fe matrix are stable, suggesting that fluctuations between these opposite states are responsible for discrepancies in experimental Mn data [?]. Recent DFT calculations using the Perdew-Burke-Ernzerhof (PBE) functional indicated that the AFM coupling phase is the ground state, while the FM coupling phase, which may be considered an excited state, resides in a rather flat local minimum in the energy landscape about 0.07 eV per Mn atom higher than the ground state [?, ?]. Further calculations within a special quasirandom structure model showed that the proportion of FM-Mn solutes is very small at the dilute limit but increases with Mn concentration, finally making the average Mn turn from negative to positive at ~6 at.% Mn [?]. These results provide a detailed scenario for Mn inversion as a function of Mn content and explain the widely scattered theoretical Mn results [?]. Two other theoretical studies predicted Mn inversion at ~13 at.% and ~1.5 at.% Mn in disordered bcc Fe-Mn alloys, respectively [?, ?].

To our knowledge, this phase transition was first proposed by Mirzoev et al. based on Tight-Binding LMTO calculations [?]. Generally speaking, little is known about this phase transition, particularly its underlying mechanism, which motivates the present study.

Early theoretical studies established that Ce, Mn, and Fe all lie at the crossover between electron bonding behavior and magnetic moment formation [?]. For these metals, the electronic delocalization-localization transition can be induced by small perturbations, ultimately modifying their properties. In this sense, a similar IPT might occur in a "simpler"metallic system with only narrow 3d bands, such as the bcc Fe-Mn solid solution, allowing the mechanism to be studied more easily. In this Letter, we demonstrate that the phase transition from AFM to FM coupling between Mn and the Fe matrix occurs at 1.85 at.% Mn based on DFT calculations using dense k-point meshes. This phase transition is confirmed to be "iso-structural," involving a shift of localized states, electron transfer, changes in bonding strength, and a sudden jump in bulk modulus. Our calculations provide a detailed view of the electronic process in this IPT, which is essential for further understanding the complex interplay between electronic and lattice degrees of freedom. Additionally, we find an excited state with FM coupling order at 1.39 at.% Mn [?]. This Letter is organized as follows: we first examine the variation of elastic and structural properties with solute content for seven Fe-X (X=3d transition metals) solid solutions. We then investigate the electronic structure and magnetism to explain the anomalous behavior in Fe-Mn alloys. An IPT is confirmed, and its mechanism is proposed. Enthalpy calculations are performed to address why only positive magnetic moments of Mn are detected experimentally at 1.85 at.% Mn and higher concentrations. Finally, we discuss the excited state at 1.39 at.% Mn, high-pressure effects, and Mn-cluster effects on this IPT.

Computational Methods

All ab initio calculations are performed using the projector augmented wave method within DFT, as implemented in the Vienna Ab initio Simulation Package (VASP) [**?**, **?**]. Exchange-correlation functionals are parameterized by Perdew and Wang (PW91) within the generalized gradient approximation [**?**], while the interpolation of the correlation part is performed using the Vosko-Wilk-Nusair (VWN) method [**?**]. The pseudopotential treating semi-core $3p^6$ electrons as valence electrons is used for Mn, while standard pseudopotentials are used for all other 3d elements. Detailed DFT settings can be found in Refs. [**?**, **?**]. Six different solute concentrations from 0.4 to 2.08 at.% are considered using six different supercells, each containing one solute atom besides Fe atoms. The dimensions of these supercells and the corresponding k-point meshes are listed in [TABLE:I]. The dense k-point meshes are necessary for accurately calculating forces on each atom and the stress tensor. For the 3\$×3×4*and*4×4×3*bccsupercells*, *thelengthratiosofthe*[100](*or*[010])*edgeversusthe*[001]*edgearesetto*3/4*and*4/ tetragonal supercell [**?**], the length ratio of the [100] edge versus the [011] (or [0 1]) edge is set to $\sqrt{2}/2$. Although slight residual stresses exist in these supercells due to the "ideal" edge-length ratio settings, they do not affect our study of the IPT mechanism in Fe-Mn alloys.

The tetrahedron smearing method with Blöchl corrections is employed for calculating electronic and magnetic properties. An arithmetic scheme is used to extract the bulk modulus B of bcc Fe-based solid solutions from the ab initio calculated stresses [**?**, **?**]. The calculated B and lattice constant a of α-Fe are listed in [TABLE:I]. Hydrostatic strain (HS) is set to \$±0.1 \$-Fe) using the same supercell and k-point mesh. Similarly, we calculate the lattice constant difference Δa of the Fe-X alloy. The elastic energy Eela is calculated as the total energy of a Fe-X alloy under -0.1% HS subtracted from that at zero strain. The substitution energy of a solute, Esub, under zero strain is defined in Ref. [**?**].

Results and Discussion

As is well established, the elastic moduli of bcc Fe-based solid solutions are linear functions of solute content, particularly at the dilute limit [**?**]. For example, the calculated bulk modulus difference ΔB values for six Fe-X (X=Ti, V, Cr, Co, Ni, and Cu) alloys decrease linearly with increasing solute content [**?**]. However, we find an exceptional case in Fe-Mn alloys. As shown by the filled circles in Figure 1: see original paper, ΔB of Fe-Mn alloy decreases linearly as Mn concentration increases from 0.4 to 1.39 at.% (note that we first focus on the ground state at 1.39 at.% Mn). However, it increases abruptly and drastically by 22.83 GPa from 1.39 to 1.85 at.% Mn, then increases slightly by 1.5 GPa at 2.08 at.% Mn. We also find that Δa of Fe-Mn alloy anomalously decreases as Mn content increases at 1.85 at.%, as shown by the filled squares in Figure 1: see original paper, while Δa of all other alloys increases linearly with increasing solutes across the entire range. Furthermore, the calculated Eela and Esub both exhibit discontinuous variations as Mn content increases from 1.39 to 1.85 at.%, as shown by the filled symbols in Figure 1: see original paper and (d), deviating from the "common linear expectations." The abrupt increase of Esub at 1.85 at.% Mn is similar to the thermodynamic anomaly of the mixing energy at ~1.5 at.% Mn predicted by LMTO calculations [**?**]. These anomalous phenomena in Fe-Mn alloys may correlate with the dual character of the 3d^5 electrons of Mn [**?**], which is unique among these 3d solutes.

The underlying mechanisms behind these anomalous phenomena can be discovered by investigating the evolution of the electronic structure with Mn concentration. First, we examine the evolution of the electron localization function (ELF) [**?**] with increasing Mn content, also comparing with six other Fe-X (X=Ti, V, Cr, Co, Ni, and Cu) alloys. The ELF values of the bonding attractors between Mn and the first as well as second nearest neighbors (1NNs & 2NNs) are both around 0.15, indicating typical metallic bonds. In the range from 0.4 to 1.39 at.% Mn, the ELF value of bonding attractors between Mn and 1NNs is ~10% less than that between Mn and 2NNs. However, they become equal at 1.85 and 2.08 at.% Mn. Figure 2: see original paper shows the shrinkage of ELF bonding domains between Mn and 2NNs as Mn increases from 1.39 to 1.85 at.%. This reflects the relative increase in the ELF value of the bonding attractors between Mn and 1NNs, indicating strengthened bonding between Mn and 1NNs. In all six other Fe-X alloys, the bonding-attractor ELF ratio between solute and 1NNs over that between solute and 2NNs remains almost constant across the entire solute concentration range. Therefore, the abrupt increases of ΔB and Eela from 1.39 to 1.85 at.% Mn might be attributed to the strengthened bonding between Mn and 1NNs. Meanwhile, the increased attraction between Mn and 1NNs compresses the Fe-Mn alloy, leading to the anomalous lattice constant decrease from 1.39 to 1.85 at.% Mn.

Additionally, we examine the magnetism evolution in Fe-Mn alloys. The magnetic moment is calculated using the standard Wigner-Seitz radius in the VASP pseudopotential database. Fe atoms show only tiny variations in magnetic moment (~2.2 B) across the entire Mn content range. Our calculated Mn is in good agreement with published data [**?**, **?**, **?**], as shown in Figure 2: see original paper. In particular, the excited state at 1.39 at.% Mn with a small positive Mn is consistent with the experimental result of ~0 B [**?**]. The Mn remains almost constant at about -1.8 B as Mn content increases from 0.4 to 1.39 at.%, but increases abruptly and drastically to 0.313 B at 1.85 at.% Mn and then remains almost constant at 2.08 at.% Mn. This suggests that solute Mn and the Fe matrix are in AFM coupling from 0.4 to 1.39 at.% Mn, but in FM coupling at 1.85 and 2.08 at.% Mn, which agrees very well with experimental results [?]. However, in the six other Fe-X (X=Ti, V, Cr, Co, Ni, and Cu) alloys, the calculated moments of solutes do not show significant variation with solute content.

Consequently, we suggest that the Fe-Mn alloy undergoes an IPT as Mn content increases from 1.39 to 1.85 at.%, evidenced by the inversion of magnetic coupling order, the strengthening of bonding between Mn and 1NNs, and the sudden jumps of ΔB and Δa. Interestingly, the increase of ΔB and decrease of Δa from the AFM phase to the FM phase can be intuitively explained by the atomic relaxations of the two phases presented by King et al. based on DFT calculations with the PBE functional (see [Figure 3: see original paper] in Ref. [?]). Their results show that in the AFM phase, Fe atoms in body-diagonal directions displace away from solute Mn over a rather long-range region, while Fe atoms in [100] and [201] directions displace toward solute Mn in a smaller region, making the lattice looser. In contrast, in the FM phase, Fe atoms displace toward solute Mn in all directions with the largest magnitude for 1NNs [?], resulting in a more compact lattice (increased ΔB and decreased Δa). The shortened distance between Mn and 1NNs reflects the strengthened bonding in the FM phase compared with the AFM phase, showing perfect consistency with our ELF calculations.

We specifically calculate the external pressure at different Mn values for the $Fe_{53}Mn_1$ system (1.85 at.% Mn) with fixed volume. This volume is an equilibrium one obtained by simultaneously optimizing ionic and magnetic configurations at zero pressure. As shown in Figure 3: see original paper, the external pressure decreases monotonically as Mn increases from -2.8 to 1.7 B, but increases slightly from 1.7 to 2.7 B. The total energy is also calculated as a function of Mn, showing a similar trend to that of Schneider et al. [?]. There is a flat local minimum around 0.2 B in the energy versus Mn curve, which might indicate an excited state. The resulting enthalpy shows a flat bottom within the Mn range from 0.7 to 1.7 B, as shown in Figure 3: see original paper, which explains why experiments under normal pressure always report positive Mn at 2.0 at.% Mn and higher concentrations.

To further understand this IPT, we examine the evolution of differential electron density diff in the (110) plane of these solutes. Here, d-iff is calculated by subtracting the electron density at a certain solute content from that at the next lower solute content, with preprocessing performed before the calculation [?]. There is only a slight change (within $±0.02e/^{3})inthe(110)ρdiffofsolutesTi,V,Cr,Co,Ni,andCuastheyincreasefrom0.4to2.08at._{2}$g bands (triply degenerate) along body diagonals to the localized e_g level (dually degenerate) along the [001] direction [?].

To test this hypothesis, we calculate the spin-polarized DOS for t_2g bands by averaging those of dzx, dyz, and dxy, and for the e_g level by averaging those of d_{z^2} and $d_{x^2-y^2}$. The e_g and t_2g DOS curves of Mn are plotted in Figure 5: see original paper and (b). As we can see, the peaks in the downward branch of t$_2$g DOS shrink while the upward e__g peak shifts to lower energy, moving below the E__F level from 1.39 to 1.85 at.% Mn. Our results showing the shrinkage of the t$_2$g peak and the simultaneous increase in e__g state density at the E__F level are similar to experimental observations of the shortening of the peak at around -2 eV and the simultaneous height increase of the peak at the E__F level in photoemission spectra during the $\gamma \rightarrow \alpha$ Ce transition [**?**]. These DOS curves correspond perfectly to the differential electron density observations; for example, the shift of the upward e__g peak from above to below the E__F level corresponds to the electron transfer at 1.85 at.% Mn in [Figure 4: see original paper]. These results confirm the electron transfer from t$_2$g bands to the e__g level. Rahman et al. also observed a similar e__g peak shift in a systematic study of DOS curves of 3d solutes in bcc Fe matrix and explained that additional 3d electrons are forced to enter the e__g majority spin states and couple ferromagnetically to the host Fe atoms [**?**].

Figure 5: see original paper shows the proportion of e__g electrons (n_{e_g}) in the total 3d electrons as a function of Mn content, presenting an abrupt increase from 1.39 to 1.85 at.% Mn. This n_{e_g} increase is very similar to that of $n_{e_g^{\uparrow}}$ in the insulator→metal transition of V$_2$O$_3$ calculated by DFT combined with dynamical mean-field theory [**?**]. Based on these DOS curves, we plot a schematic of 3d electron transfer from the lower t$_2$g bands to the upper e__g level in Figure 5: see original paper, which thoroughly explains the abrupt Esub increase as Mn increases from 1.39 to 1.85 at.% in Figure 1: see original paper.

Interestingly, according to the band structure theory suggested by Goodenough [**?**], it is the 3d electron transfer that gives rise to the inversion of magnetic coupling order and the concomitant Fe-Mn bond strengthening. From 0.4 to 1.39 at.% Mn, solute Mn is in AFM coupling with the Fe matrix because the e__g level is filled with very few electrons but not empty. Meanwhile, the bonding half of the t$_2$g band is filled, and the antibonding half is partially filled. As Mn increases to 1.85 at.%, the electron transfer makes the bonding half of the t$_2$g band remain filled or very close to filled, but the antibonding half becomes empty, leading to Fe-Mn bond strengthening. Furthermore, the upward branch of the e__g level becomes filled or close to filled at 1.85 at.% Mn, leading to FM coupling between Mn and the Fe matrix. In this sense, the decreased occupation of the t$_2$g state corresponds to bond strengthening between Mn and 1NNs, and the increased occupation of the e__g level corresponds to the FM coupling order. Therefore, the proportion of e__g electrons, n_{e_g}/n_{3d}, might serve as the order parameter of this IPT.

Finally, we discuss three issues. The first concerns the excited state (FM phase) at 1.39 at.% Mn. Figure S7 displays 3d DOS curves, ELF domains, and differential electron density contours (the FM phase minus the AFM phase with Mn ~ -1.8 B) on the (110) plane of Mn [**?**], which are very similar to their counterparts in the FM phase at 1.85 at.% Mn. Hence, this excited state essentially possesses the elastic, structural, and electronic properties of the FM phase. Our calculated Esub of Mn in this excited state is ~0.05 eV higher than that in the AFM phase at 1.39 at.% Mn. An experimental Mn of ~0 B was observed at 1.5 at.% Mn under ambient conditions [?], which might indicate that this excited state is reached, albeit with small probability. Additionally, our calculations show that only this excited state exists under pressures above 10.0 kBar at 1.39 at.% Mn [?]. Secondly, when the Fe$_{53}$Mn$_1$ system is under a -2.0% volumetric strain, the two local minima at -1.3 B (46.4 kBar) and 0.7 B (40.3 kBar) have similar energies, as shown in Figure 3: see original paper. Our calculations on the Fe$_{53}$Mn$_1$ system show that above 37.0 kBar, the enthalpy of the FM phase is lower than that of the AFM phase with Mn ~ -1.8 B [?]. These results demonstrate that the FM phase is the ground state under high pressure at 1.85 at.% Mn. The third issue concerns the Mn-cluster effect on this IPT. We calculate ΔB at 1.56 at.% Mn using Fe$_{126}$Mn$_2$ systems with various Mn-pair configurations at zero pressure [?]. The ΔB values with Mn-pairs forming from the first to the fourth nearest neighbors (1NN–4NN, see Ref. [?]) lie very close to the line before the IPT, while that with the 5NN Mn-pair lies on the line after the IPT, as shown in Figure S10 in Ref. [?]. For configurations in which the Mn-pair distances are farther than that of 5NN, ab initio calculations cannot converge under the prescribed force criterion (\$ \$0.002 eV/Å per atom). Nonetheless, under a relaxed criterion of \$ \$0.004 eV/Å per atom, the calculations converge only for two configurations: “far1” denoting the [100] Mn-pair of 2a length, and “far2” denoting the [111] Mn-pair of $\sqrt{3}$a length. As can be seen, ΔB values of “far1” and “far2” lie close to the lines after and before the IPT, respectively. From these results, we conclude that Fe$_{126}$Mn$_2$ systems with Mn-pair configurations of 5NN and “far1” are both in the FM phase.

In summary, our DFT calculations using dense k-point meshes describe two distinct solutions (phases) of dilute bcc Fe-Mn alloys and capture an iso-structural phase transition (IPT) between them. This IPT originates from the main peak of the 3d e_g state shifting across the Fermi level. The mechanism emphasizes that the dual character of the 3d^5 electrons of Mn is driven by intra-atomic electron transfer between the itinerant t$_2$g band and the localized e_g level. This IPT can be induced by changing Mn content or external pressure. The phase transition implies a sudden jump in bulk modulus, an inversion of magnetic coupling order between solute Mn and the Fe matrix, and a change in bonding strength between Mn and its first-nearest-neighbor Fe atoms. Our study provides a comprehensive view of the electronic process in this IPT, which is enlightening for understanding the mechanisms of other similar correlation-driven phase transitions. Our results also indicate that bcc Fe-Mn alloys might have a more complex phase diagram than currently known.

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[31] See Supplementary Material in the same Submission, which includes additional information on: (i) bulk modulus variation with solute content of 7 Fe-X (X=3d transition metals) alloys; (ii) determination of magnetic coupling phase at 6 Mn concentrations; (iii) electronic and magnetic properties of the ferromagnetic phase at 1.39 at.% Mn; (iv) enthalpy variation with pressure of $Fe_{53}Mn_1$ system in ferromagnetic phase; (v) elastic, structural and magnetic properties of $Fe_{126}Mn_2$ system.
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Captions

TABLE I: Solute contents (at.%) of six solid-solution systems, dimensions, and corresponding k-point meshes. All k-point meshes are Γ-centered. For the first five supercells, dimensions are in multiples l, m, and n of a two-atom bcc cell along the [100], [010], and [001] directions, respectively; for the last supercell, dimensions are in multiples l, m, and n of a four-atom tetragonal cell (see Figure 1: see original paper in Ref. [**?**]) along the [100], [011], and [0 1] directions, respectively. Herein X denotes solute; l, m, and n are integers. The calculated lattice constant a_0 (unit: Å) and bulk modulus B (unit: GPa) of α-Fe for each supercell and k-point mesh are also shown. The effect of Pulay stress on a_0 and B is corrected [**?**].

FIG. 1: (Color online) Variations of (a) bulk modulus change ΔB, (b) lattice constant change Δa, (c) elastic energy Eela, and (d) substitution energy Esub as Mn content increases. The excited state at 1.39 at.% Mn is represented by half-filled symbols. Lines are linear fits. The Eela values are for systems with 250 atoms at each Mn content.

FIG. 2: (Color online) (a) Domains of electron localization function (ELF) between Mn (purple ball at center) and the first as well as second nearest neigh-

bors (1NNs & 2NNs, brown balls; 2NNs are not shown) at 1.39 and 1.85 at.% Mn. The left picture shows the antiferromagnetic phase at 1.39 at.% Mn. The ELF value is set to that of the attractors between Mn and 1NNs. (b) The magnetic moment of Mn (Mn) versus its content. The excited state at 1.39 at.% Mn is represented by the half-filled circle. Published data are from Refs. [**?**, **?**, **?**, **?**, **?**, **?**].

FIG. 3: (Color online) (a) External pressure (P), (b) relative total energy (ΔE), and (c) relative enthalpy (ΔH) as a function of magnetic moment of Mn in the $Fe_{53}Mn_1$ system. Red open squares and blue open circles denote results at equilibrium volume and at a volumetric strain of -2.0%, respectively. The ΔE and ΔH values are relative to those at -1.3 and 1.2 B, respectively. Thin broken horizontal lines denote the altitudes of local minima.

FIG. 4: (Color online) Differential electron density on the (110) plane of Mn in bcc Fe-Mn alloy from 0.4 to 2.08 at.% Mn. The unit of electron density is e/Å^3. In all pictures, Mn atoms are placed at the center. In the leftmost picture, the four black dots mark the first nearest neighbor Fe (1NN).

FIG. 5: (Color online) Spin-polarized DOS curves of (a) 3d t_2g and (b) 3d e_g states of Mn at different Mn contents. At 1.39 at.% Mn, only the antiferromagnetic DOS curves are shown. (c) The proportion of e_g electron number to total 3d electron number as a function of Mn content. (d) Schematic of electron transfer within 3d states. The blue arrow indicates the electron transfer direction. The magenta and red arrows denote the upward spin of the e_g state and downward spin of the t_2g state, respectively.

Note: Figure translations are in progress. See original paper for figures.

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