Neutron diffraction evidence for local spin canting, weak Jahn–Teller distortion, and magnetic compensation in Ti$_{1-x}$Mn$_x$Co$_2$O$_4$ spinel

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Abstract

A systematic study using neutron diffraction and magnetic susceptibility is reported on Mn substituted ferrimagnetic inverse spinel Ti$_{1-x}$Mn$_x$Co$_2$O$_4$ in the temperature interval $1.6 \leq T \leq 300$ K. Our neutron diffraction study reveals cooperative distortions of the $T$O$_6$ octahedra in the Ti$_{1-x}$Mn$_x$Co$_2$O$_4$ system for all the Jahn–Teller active ions $T = \text{Mn}^{3+}$, $\text{Ti}^{3+}$ and $\text{Co}^{3+}$, having the electronic configurations $3d^1$, $3d^4$ and $3d^6$, respectively which are confirmed by the x-ray photoelectron spectroscopy. Two specific compositions ($x = 0.2$ and 0.4) have been chosen in this study because these two systems show unique features such as; (i) noncollinear Yafet–Kittel type magnetic ordering, and (ii) weak tetragonal distortion with $c/a < 1$, in which the apical bond length $d_{ab}(T_{B}-O)$ is longer than the equatorial bond length $d_{ab}(T_{B}-O)$ due to the splitting of the $e_g$ level of Mn$^{3+}$ ions into $d_{x^2-y^2}$ and $d_{z^2}$. For the composition $x = 0.4$, the distortion in the $T_{B}O_6$ octahedra is stronger as compared to $x = 0.2$ because of the higher content of trivalent Mn. Ferrimagnetic ordering in Ti$_{0.6}$Mn$_{0.4}$Co$_2$O$_4$ and Ti$_{0.8}$Mn$_{0.2}$Co$_2$O$_4$ sets in at $110.3$ and $78.2$ K, respectively due to the presence of unequal magnetic moments of cations, where Ti$^{3+}$, Mn$^{3+}$, and Co$^{3+}$ occupy the octahedral, whereas, Co$^{2+}$ sits in the tetrahedral site. For both compounds an additional weak antiferromagnetic component could be observed lying perpendicular to the ferrimagnetic component. The analysis of static and dynamic magnetic susceptibilities combined with the heat-capacity data reveals a magnetic compensation phenomenon (MCP) at $T_{\text{COMP}} = 25.4$ K in Ti$_{0.8}$Mn$_{0.2}$Co$_2$O$_4$ and a reentrant spin-glass behaviour in Ti$_{0.6}$Mn$_{0.4}$Co$_2$O$_4$ with a freezing temperature of $\sim 110.1$ K. The MCP in this compound is characterized by sign reversal of magnetization and bipolar exchange bias effect below $T_{\text{COMP}}$ with its magnitude depending on the direction of external magnetic field and the cooling protocol.

Keywords: neutron diffraction, ferrimagnetism, Jahn–Teller distortion, magnetic compensation, spin-glass

(Some figures may appear in colour only in the online journal)
1. Introduction

Competing magnetic exchange interactions between the cations in spinel oxides $AB_2O_4$ play a major role in deciding their magnetic and crystal structure along with various other physical properties [1–8]. The contribution of orbital degeneracy under very high crystal-field ($>2.36$ eV), Hund’s exchange couplings ($<0.7$ eV) and spin–orbit interactions ($5.5$ eV) leads to some interesting properties like spin-liquid state, magnetothermal, anisotropic magnetoelastic, magnetoelectric, and magnetostructural distortion driven by cooperative Jahn–Teller effect [2, 5, 6, 9–15]. In particular, giant magnetic anisotropy ($650$ kOe) and atomic displacements, negative-magnetization with compensation phenomena, zero-field cooled bipolar exchange-bias effect and reentrant spin-glass behavior in few Mn-, Co- and Cr-based spinels has drawn immense attention [16–21]. Exploring the tunability of such exotic properties may lead to potential applications in magnetic read/write heads, spin-valves and other switching devices [22–25].

Precise understanding of the cationic distribution using the neutron diffraction studies in diluted magnetic spinels is a challenging issue. For example, earlier studies related to the dilution of $CoO_4$ at octahedral sites with Mg (ionic radius $r_{Mg}=0.57$ Å) reveals that there is a limit to the occupancy of the $Mg^{2+}$ ions at tetrahedral sites [26]. Such dilution (with tetravalent nonmagnetic elements like Sn$^{4+}$, Ge$^{4+}$ or Ti$^{4+}$) play a major role in the disruption of antiferromagnetic ordering in $CoO_4$ and results in a short-range ordering with reentrant spin-glass (RSG) behavior [19, 20, 27, 28]. Coexistence of ferrimagnetic behaviour with RSG, negative magnetization below the compensation temperature and giant asymmetry in the hysteresis loops are some of the important features noticed below the compensation temperature and giant asymmetry in ferrimagnetic behaviour with RSG, negative magnetization below the compensation point and bipolar exchange bias under zero-field-cooled (ZFC) condition [19, 20, 39]. Moreover, the inverse spinel $MnO_2$ exhibits only ferrimagnetic behavior, without any of the above mentioned characteristics. Since both the end compounds exhibits very different magnetic ground state it is worth to investigate the magnetic and crystal structures of the intermediate compositions of these two end compounds. Another motivating factor in investigating this system is to probe the magnitude of permanent magnetic moment on the trivalent $B$ site Co ions which usually do not exhibit any magnetic moment due to the large crystal-field splitting ($\geq19.000$ cm$^{-1}$) of the 3$d$ orbitals by the octahedral cubic field [9]. Therefore, motivated by the wide range of applications and unique magnetic characteristics of $MnO_2$ and $TiO_2$ compounds, an attempt has been made in the present work to investigate a detailed crystal structure and magnetic ordering of $Ti_{1-x}Mn_xCo_2O_4$ polycrystalline samples using neutron powder diffraction and dc- and ac-magnetization measurements. Among various compositions ($0 \leq x \leq 1$) that we prepared, two specific compositions $Ti_{0.3}Mn_{0.2}Co_2O_4$ and $Ti_{0.6}Mn_{0.2}Co_2O_4$ are chosen for a detailed study because they show the evidence for magnetic compensation effect, reentrant spin-glass behavior and exchange-bias effect.

Based on the characterization results; (i) we examine the following statistical distribution of cationic occupancy ($Co^{2+}$)$_x$ ($Ti^{4+}$)$_{1-x}$ ($Mn^{2+}$)$_x$ ($Co^{4+}$)$_{1-x}$ ($O_2$)$_4$ and ($Co^{2+}$)$_x$ ($Ti^{4+}$)$_{1-x}$ ($Mn^{4+}$)$_x$ ($Co^{3+}$)$_{1-x}$ ($O_2$)$_4$; (ii) large bipolar exchange-bias fields ($3.6$ kOe at $T = 15$ K), (iii) negative magnetization ($-0.67$ emu/g at $T = 5$ K), and (iv) magnetic compensation phenomena ($T_{comp} \sim 25$ K) for $x = 0.2$, and (v) the determination of the ordered magnetic moment values and valencies of the individual metal ions using spinel mixed oxides.

2. Experimental details

Polycrystalline samples of Mn doped $TiCo_2O_4$ were fabricated using the standard solid-state-reaction method using stoichiometric amounts of the precursors $TiO_2$, $MnO_3$, and $CoO_2$. These mixed oxides were grounded in an agate mortar for 6h and pelletized using a hydraulic press with 50kN pressure followed by sintering at 1100 °C for 8h duration with 4 °C per minute heating and cooling rates. Structural characterization and phase purity of the sintered pellets were investigated by x-ray diffraction (XRD) measurements, performed using a Rigaku x-ray diffractometer (model: TRAX III) with Cu-Kα radiation ($\lambda = 1.54056$ Å). The XRD patterns of $Ti_{1-x}Mn_xCo_2O_4$ were very similar to the end member $TiCo_2O_4$ (space group $Fd\bar{3}m$ (No. 227)). However, a slight decrease in the lattice parameter was noticed with increasing the Mn concentration ($a = 8.384$ Å, for $x \sim 0.2$) due to smaller ionic size of the Mn ($r \sim 0.645$ Å) as compared to Ti ($r \sim 0.67$ Å).
Neutron powder diffraction experiments on Ti0.8Mn0.2Co2O4 and Ti0.6Mn0.4Co2O4 were carried out on the instruments E2, E6, and E9 at the BER II reactor of the Helmholtz-Zentrum Berlin. The instrument E9 uses a Ge monochromator selecting the neutron wavelength $\lambda = 1.3083\ \text{Å}$, while the instruments E2 and E6 use a pyrolytic graphite (PG) monochromator selecting the neutron wavelengths $\lambda = 2.379$ and $2.423\ \text{Å}$, respectively. On these instruments powder diffraction patterns were recorded between the following diffraction angles: between 14.7 and 90.2° (E2), 5.5 and 136.6° (E6), and 5 and 141.8° (E9). For both compounds Ti0.8Mn0.2Co2O4 and Ti0.6Mn0.4Co2O4 the crystal structure parameters at 3 K were investigated from data sets collected on E9. An additional neutron diffraction pattern from Ti0.6Mn0.4Co2O4 sample was collected for sake of comparison at 295 K. In order to investigate in detail the magnetic structure neutron powder diffraction patterns were collected at $T = 2\ \text{K}$ on the instrument E2 with high counting statistics (24h/pattern) using a 15 min collimation to improve the instrumental resolution. In the paramagnetic range a second powder pattern of Ti0.8Mn0.2Co2O4 and Ti0.6Mn0.4Co2O4 was collected at 90 and 142 K, respectively.

The temperature dependent behaviour of the magnetic ordering of both spinels has been investigated on the instrument E6. The refinements of crystal and magnetic structures were carried out with the FullProf program [40]. The nuclear scattering lengths $b(\text{O}) = 5.805\ \text{fm}$, $b(\text{Ti}) = -3.30\ \text{fm}$, $b(\text{Mn}) = -3.73\ \text{fm}$, and $b(\text{Co}) = 2.50\ \text{fm}$, were used [41]. The magnetic form factors of the Ti3+, Mn3+, Co2+, and Co3+ ions were taken from [42].

For the electronic structure and elemental analysis, we performed x-ray photoelectron spectroscopy (XPS) measurements using Al-Ko lab source. All the data was recorded using an Omicron hemispherical analyzer. After subtracting the Tougaard background, all the XPS core-level data were fitted with mixed Lorentzian–Gaussian profiles. The superconducting quantum interference device (SQUID) based magnetometer (MPMS: magnetic property measurements system) with working temperature range 4–300 K and magnetic field ($H$) up to $\pm 50\ \text{kOe}$ was used for the magnetization measurements. Temperature dependence of specific heat $C_p(T)$ was recorded by means of a physical-property-measurement-systems (PPMS) from quantum design.

3. Results and discussion

3.1. Crystal structure

The inverse spinel Co3TiO4 was found to crystallize in the cubic space group $Fd\overline{3}m$ (No. 227) [20]. Usually in normal spinels with the general formula $AB_2O_4$, the $A^2+$ ions are located on the tetrahedral site (A site), while the $B^3+$ ions are located on the octahedral site (B site). In TiCo2O4 the cobalt ions have the valence 3+ and 2+, and therefore it can be expected that Co3+ at the A site (labelled as CoA) is located at the Wyckoff position $8b(3\frac{1}{2}, 3\frac{1}{2}, 3\frac{1}{2})$, while Co3+ occupy one half of the B site (labelled as CoB) located at $16c(0, 0, 0)$. Consequently, the titanium ions are expected to have the valence 3+ and occupy the other half of the B site. Further the oxygen atoms occupy the position $32e(x, x, x)$. The formula of this inverse spinel can be given as Co(Co0.5Ti0.5)2O4. Accordingly, we have refined the crystal structure of Ti0.8Mn0.2Co2O4 and Ti0.6Mn0.4Co2O4 (or in detail Co(Ti0.8Mn0.2Co2)O4 and Co(Ti0.6Mn0.4Co2)O4) in the cubic space group $Pm\overline{3}m$. In order to determine the correct composition, we have refined the site occupancies of both compounds from data sets collected on E9. Due to the fact that manganese and titanium have negative neutron scattering lengths it was possible to determine the occupancies with good accuracy. In the first step the occupancies of the Co2+ ions at the A site and the oxygen atoms were refined, while the occupancies of the B-site atoms were fixed. This could improve the fit with the consequence that the obtained occupancies of both Co2+ and O were found to be too small. On the other hand, it is important to note that the ratio $occ(O)/occ(Co^{2+})$ reached a value 4.11(3) which is slightly larger than the ideal value 4. This indicates that the sample does not show an oxygen deficiency. In a further refinement we assumed that Mn atoms are also located at the A site. It was found that only a negligible amount $\sim 1.1(5)\%$ of manganese could be located at this site. This shows that the A site is practically fully occupied with Co3+. This was also found earlier for the compound MnCo2O4 [43]. In the next refinement the occupancies of Co3+ and O were fixed. Here one finds a reduced scattering power at the B site which indicates that the manganese and titanium content at the B site is higher than that of cobalt. The loss of cobalt can be explained by the fact that both samples contain minor impurities of CoO4. On the basis of accurate weighting of the components we finally used the constraint for the B site $(1 + x)\ [occ(\text{Ti}) + occ(\text{Mn})] + (1 - x) \ occ(\text{Co}) = 1$, where $occ$ is the nominal content at the B site. Finally, from the data sets collected for $x = 0.4$ at $T = 3$ and 295 K we found the chemical compositions are (Co3+)4 $[\text{Ti}_{0.629(5)} \text{Mn}_{0.420(5)} \text{Co}_{0.945(5)}]\text{O}_4$ and (Co2+)4 $[\text{Ti}_{0.633(5)} \text{Mn}_{0.422(5)} \text{Co}_{0.951(5)}]\text{O}_4$, respectively. For the other sample with $x = 0.2$ the chemical composition was found to be (Co2+)4 $[\text{Ti}_{0.841(5)} \text{Mn}_{0.201(5)} \text{Co}_{0.945(5)}]\text{O}_4$.

Despite the fact that we could not observe a peak broadening of particular reflections, we also tried to carry out the refinements of the crystal structure in the next lower symmetric space group $R3m$ (No. 141, cell choice 2) with the cell dimensions $a_0 \times b_0 \times c_0 = a_0\sqrt{3} \times b_0\sqrt{3} \times c_0$. In this setting the Co2+ ions at the A site (labelled as CoA) are located at the Wyckoff position $4b(0, \frac{1}{2}, \frac{1}{2})$, while at the B site the Ti3+, Mn3+, and the other half of the Co (here as Co3+ and labelled as CoB) are located at $8c(0, 0, 0)$. The oxygen atoms occupy the position $16d(0, y, z)$, where $y$ and $z$ approximately have the values 0.5 and 0.25, respectively. However, we found from the Rietveld refinements of Ti0.6Mn0.4Co2O4 system $clav\sqrt{2}$ ratios to be 0.9988(3) and 0.9995(3) at 3 and 295 K, respectively. Similarly, $clav\sqrt{2}$ ratio for Ti0.8Mn0.2Co2O4 at 3 K was found to be 0.9988(3). These values indicate the presence of a weak tetragonal distortion at low temperature in the magnetically ordered region. The results of the Rietveld refinements are given in table 1 and figure 1. For the Co2+ ions at the A site, which have the 3$d^6$ configuration, cooperative distortions of the CoO4 tetrahedra through the Jahn–Teller
Table 1. Results of the Rietveld refinements of the neutron powder diffraction data of Ti$_{0.8}$Mn$_{0.2}$Co$_2$O$_4$ and Ti$_{0.6}$Mn$_{0.4}$Co$_2$O$_4$ collected on the instrument E9 at 3 K. The refinements were carried out in the tetragonal space group $I_4_1/amd$. The given residuals are defined as $R_F = \sum|F_{o}-|F_{c}|/\sum|F_{o}|$. Listed are the positional parameters $y$ and $z$ of the O atom located at the site 16b(0, y, z) and the occupancies of the Ti$_{\text{occ}}$, Mn$_{\text{occ}}$, and Co$_{\text{occ}}$ atoms at the site 8c(0,0,0). For all atoms an overall thermal parameter $B_{\text{iso}}$ was refined. Further the bond distances in the $T_b$O$_6$ octahedra ($T_b = $ Ti$_{\text{B}}$, Mn$_{\text{B}}$, and Co$_{\text{B}}$), and the Co$_2$O$_4$ tetrahedra as well as the lattice parameters are also given.

|                | Ti$_{0.8}$Mn$_{0.2}$Co$_2$O$_4$ | Ti$_{0.6}$Mn$_{0.4}$Co$_2$O$_4$ |
|----------------|---------------------------------|---------------------------------|
| $T$ [K]        | 3                               | 3                               |
| $\alpha c(TI_b)$ | 0.835(4)                        | 0.618(3)                        |
| $\alpha c$(Mn$_{\text{B}}$) | 0.209(4)                        | 0.412(3)                        |
| $\alpha c$(Co$_{\text{B}}$) | 0.956(4)                        | 0.970(3)                        |
| $y$(O)         | 0.5218(5)                       | 0.5241(4)                       |
| $z$(O)         | 0.2398(5)                       | 0.2414(5)                       |
| $\alpha$(A)    | 5.9499(4)                       | 5.9231(4)                       |
| $c_1$(Å)       | 8.4044(10)                      | 8.3677(11)                      |
| $c_1\alpha\sqrt{2}$ | 0.9988(3)                       | 0.9988(3)                       |
| $V$(Å$^3$)     | 297.53(5)                       | 293.57(6)                       |
| $B_{\text{iso}}$(Å$^2$) | 0.37(5)                         | 0.53(6)                         |
| $d_{\text{TB}-(T-O)}<2$ | 2.020(5)                       | 2.025(4)                       |
| $d_{\text{Co4x-O}<4}$ | 1.976(4)                       | 1.972(3)                       |
| $R_F$          | 0.042                           | 0.042                           |

effect are absent. This is not the case for the TO$_6$ octahedra, which contain the Jahn–Teller active ions Ti$^{3+}$, Mn$^{3+}$ and Co$^{3+}$, having the 3$d^1$, 3$d^2$ and 3$d^6$ configurations, respectively. For the Mn$^{3+}$, Ti$^{3+}$ and Co$^{3+}$ ions electronic energy can be gained if the 2$t_g$ levels split into a lower $d_{z^2}$ level and a higher twofold degenerate $d_{xy}$, $d_{xz}$, $d_{yz}$ levels (figure 2). This would lead to a tetragonal distortion with a $c/a$ ratio smaller than 1, and also a shrinking of the apical bond length ($d_{\text{TB}-(T-O)}$) (figure 2). But the crystal structure refinements of Ti$_{0.8}$Mn$_{0.2}$Co$_2$O$_4$ showed that the apical bond length ($d_{\text{TB}-(T-O)} = 2.020(5)$ Å is slightly longer than the equatorial one ($d_{\text{TB}-(T-O)} = 2.016(2)$ Å. This effect is stronger in Ti$_{0.6}$Mn$_{0.4}$Co$_2$O$_4$, where the Mn content is twice that in Ti$_{0.8}$Mn$_{0.2}$Co$_2$O$_4$, in which the bond lengths are $d_{\text{TB}-(T-O)} = 2.025(4)$ Å and $d_{\text{TB}-(T-O)} = 1.998(2)$ Å. Practically the same values are obtained if we assume $c/a$ ratio equal to 1. Here it is interesting to note that a tetragonal distortion could not be detected in TiCo$_2$O$_4$ [20] suggesting that the Jahn–Teller activity of the Ti$^{3+}$ and Co$^{3+}$ ions is rather weak in this system. Therefore, we can assume that the elongation of the apical bond $d_{\text{TB}-(T-O)}$ can be ascribed to the Jahn–Teller activity of the Mn$^{3+}$ ions having the 3$d^6$ configuration. In this case electronic energy can be gained if the $e_g$ level splits into $d_{xz}$, $d_{yz}$ and $d_{z^2}$ levels, where the fourth electron occupies lower lying $d_{z^2}$ level. This electronic configuration finally leads to an elongation of the TO$_6$ octahedra along the $c$ axis. Possibly the Jahn–Teller effect on the two ion acts along different directions as found earlier in Ni$_{1-x}$Cu$_x$Cr$_2$O$_4$ system [5] and leads to compensation of particular distortions.

3.2. Magnetic ordering

Figure 3 shows the powder neutron diffraction patterns of Ti$_{0.8}$Mn$_{0.2}$Co$_2$O$_4$ and Ti$_{0.6}$Mn$_{0.4}$Co$_2$O$_4$ collected on the instrument E2 well below and above the magnetic ordering

Figure 1. Rietveld refinements of the neutron powder diffraction data of (a) Ti$_{0.8}$Mn$_{0.2}$Co$_2$O$_4$ and (b) Ti$_{0.6}$Mn$_{0.4}$Co$_2$O$_4$ collected on E9 (wavelength, $\lambda = 1.3083$ Å) at 3 K. The crystal structure was refined in the tetragonal space group $I_4_1/amd$. The calculated patterns (red) are compared with the observed one (black circles). In the lower part of each diagram the difference pattern (blue) as well as the positions of the nuclear (N) and magnetic (M) reflections are shown. A strongest magnetic contribution is observed for the reflections 101 and 200/112 (see also figure 3).
the Jahn–Teller effect. I
metric tetragonal space group e
Ti1
temperature
Figure 2.
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are indexes as 110 and 002. Thus the presence of magnetic intensity suggests loss of at least one of the d-glade planes indicating the presence of an additional antiferromagnetic (AF) component.

Using the tetragonal setting the obtained splitting of the individual reflections 110 and 002 is too weak to distinguish their magnetic contributions. Consequently, it was not possible to determine the directions of the AF and FI components. However, it was possible to determine the spin sequence of the B-site atoms CoB, TiB, and MnB atoms located at the positions (1) 0,0,0; (2) 1/2,1/2,1/2; (3) 1/2,1/2,0; (4) 1/2,1/2,1/2. In general, the possible spin sequences for the B-site atoms are + + + +, + − − −, + + − −, and + + + −. For the determination of the magnetic structure we fixed the moment of the ferromagnetic (F) component to be aligned parallel to the a axis. Several tests have shown that the best fit was achieved using the sequences + + + − and + + + + for the AF components aligned parallel to the b and c axes, respectively. These modes are compatible with those of the irreducible representation (irrep) Γ8 obtained from the representation analysis using the program BasIrep of the Fullprof suite [20]. This irrep is of dimension 3 and it appears 2 times in Γ5 which means that the ferromagnetic component can be alternatively aligned parallel to b and c. It can be seen in figure 4 that AF coupled moments show a non collinear magnetic ordering, where in the present setting the moment points along [011] and [01−1], respectively. A coexistence of AF and FI ordering was also observed in the system Ni1−xCuxCr2O4 [5], where the FI ordering occurs in the ab plane and the AF component is aligned parallel to the c axis.

Both the magnetic ions Mn3+ and Co3+ in the 3d4 and 3d6 configurations have four unpaired electrons in the high-spin state, while Ti3+ ions in the 3d3 has only one electron. Therefore, the expected theoretical magnetic moment values for the high-spin state are µeff = g S µB = 4.0 µB for Mn3+ and Co3+, and µeff = g S µB = 1.0 µB for Ti3+. At this point it is worth to mentioned that the total moments of the ions at the B site can differ, especially due to the presence of spin–orbital coupling. Nevertheless, we have tried to estimate the individual moment values at the B site using the constraint µ(Mn3+) = µ(Co3+) = 4 × µ(Ti3+). The results of the refinements are given in table 2. The obtained total moments of the Ti3+ ions vary in both compounds between 0.52 and 0.60 µB, and those of the Mn3+/Co3+ ions between 2.09 and 2.39 µB, which are considerably smaller than the theoretical values given above. It has been mentioned above that the magnetic moments of the B site Co3+ ions were found to be zero in Co3O4 and MnCo2O4 [9, 33], while in the case of TiCo2O4 they are also magnetically ordered [20]. In order to estimate the magnetic moments of Co3+ we used the fixed moment value 3.84 µB of Mn3+ as determined earlier for MnCo2O4 [33]. From the refinements, we now used the constraint µ(Mn3+) = 4 × µ(Ti3+), magnetic moment values of Co3+ vary between 0.75 and 0.80 for Ti0.8Mn0.2Co2O4.

For Ti0.6Mn0.4Co2O4 the values, which vary between 0.61 and 0.65 µB, are found to be smaller. This may give the trend that the moment of Co3+ ion decreases with increasing Mn content. The Co3+ ion at the A site have three unpaired electrons
in the 3d⁺ configuration. Here the magnitude of magnetic moment reaches between 2.60 and 3.10 \( \mu_B \), which are close to the theoretical value of the high-spin state \( \mu_{\text{eff}} = g S \mu_B = 3.0 \mu_B \). In contrast the moment of Co²⁺ ion at the A site in TiCo₂O₄ was found to be reduced which can be ascribed to stronger frustration effects [20].

In table 2 we also compare the resulting ferromagnetic components of Ti₀.₈Mn₀.₂Co₂O₄ and Ti₀.₆Mn₀.₄Co₂O₄ determined from magnetization measurement with those obtained from our neutron diffraction study given as \( 2\mu_{\text{FI}}(T_B) - \mu_{\text{AF}}(T_B) \). Due to the fact that the resulting ferromagnetic components are relatively small we were not able to determine them with good accuracy from our neutron diffraction data. Taking this into account the moment values obtained from both methods show more or less a good agreement (table 2). We further have investigated the thermal variation of the magnetic moments of Ti₀.₈Mn₀.₂Co₂O₄ and Ti₀.₆Mn₀.₄Co₂O₄. Due to the fact that the AF component could not be precisely determined from the E6 data in the temperature range close to the Curie temperature we used the ratio \( \mu_{\text{FI}}(T_B)/\mu_{\text{AF}}(T_B) \) as constraint. As given above we were not able to determine precisely the individual moment values of Ti³⁺, Mn³⁺, and Co³⁺ at the B site. Therefore, only the averaged moment values at the B site (labelled as \( T_B \)) are plotted in figure 5 which are coupled ferrimagnetically with the moment values at the A site (labelled as \( \text{Co}^\text{A} \)).

We also studied the temperature variation of the peak shape. For the Rietveld refinements we used the pseudo-Voigt function which is defined as \( pV(x) = \eta L(x) + (1 - \eta) G(x) \), where...
to estimate the moment of $Co^{3+}$ 

The magnetic ordering temperature $T_{m}$ for $Ti_{0.6}Mn_{0.4}Co_{2}O_{4}$ is strongly 
varying with the temperature reaching finally a 

The changes of the peak shape can be 

such case the correlation length should consist of two 

limited ferrimagnetic clusters below a critical composition 

clusters, together with a diffuse scattering occurring from the 

chemical percolation approach reported by Cowley 

peak shape may also describe the distribution of the magnetic 

network and a glassy state, respectively [45]. Such disordered 

spins do not give any contribution to magnetic Bragg intensities. 

Neutron diffraction studies of systems like $Fe_{0.5}Mg_{0.5}Cl_{2}$ and $Fe_{0.8}Mg_{0.2}Cl_{2}$ reported the existence of magnetic diffuse scattering due to the coexistence of antiferromagnetic long-range ordering and a transverse spin-glass state [46, 47]. The appearance of superimposed magnetic diffuse scattering at the antiferromagnetic Bragg peak indicates the changes taking place in local magnetic ordering. It is also reported that the intensity of such diffuse scattering changes drastically with decreasing temperature, while the intensity of the antiferromagnetic Bragg peak slightly decreases [46, 47]. In the 1980s the existence of a mixed phase (spin-glass and ferris/ferro/antiferromagnetic orderings) system lead to controversial discussion. There is a fair amount of debate on the nature of this magnetic order till date despite many advances in the condensed matter theory which predicts various forms of reentrant behavior (in both Ising and Heisenberg systems) [48–51]. Wong et al reported the coexistence of spin-glass and antiferromagnetic orders in the Ising system $Fe_{0.55}Mg_{0.45}Cl_{2}$ [47]. In order to probe precisely the transverse spin-glass nature of this system these authors recorded diffuse scattering scans at 

1.5 K along the three different crystallographic directions below the freezing temperature ($\sim 3$ K). Consequently, they observed a superimposed Lorentzian diffuse magnetic peak at the position of the nuclear Bragg peak with the correlation length $\xi \sim 10$ A. Such frozen short-range correlation is probably the source of the spin-glass behavior observed in single crystals of $Fe_{0.55}Mg_{0.45}Cl_{2}$ [47]. Considering these results, in the present case we performed a detailed ac-magnetic susceptibility and diffuse neutron scattering studies to probe the reentrant glassy behavior.

Figure 7 shows an enlarged view around the base of the 111 neutron-diffraction peak of $Ti_{0.6}Mn_{0.4}Co_{2}O_{4}$ and $Ti_{0.6}Mn_{0.4}Co_{2}O_{4}$, well below (at 1.7 K / 2 K) and above (at

| Magnetic moment | $Ti_{0.2}Mn_{0.8}Co_{2}O_{4}$ | $Ti_{0.4}Mn_{0.6}Co_{2}O_{4}$ | $Ti_{0.6}Mn_{0.4}Co_{2}O_{4}$ | $Ti_{0.8}Mn_{0.2}Co_{2}O_{4}$ |
|-----------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| $\mu_{TB}(Co^{3+}) [\mu_B]$ | E2                        | E6                        | E2                        | E6                        |
| $\mu_{TB}(Mn^{3+}/Co^{3+}) [\mu_B]$ | 2.60(3)                  | 2.99(2)                  | 2.94(4)                  | 3.10(3)                  |
| $\mu_{TB}(Ti^{3+}) [\mu_B]$ | 2.09(5)                  | 2.29(4)                  | 2.13(4)                  | 2.39(4)                  |
| $\mu_{TB}(Fe^{3+}) [\mu_B]$ | 1.43(3)                  | 1.57(3)                  | 1.63(3)                  | 1.82(3)                  |
| $\mu_{TB}(Fe^{3+}) [\mu_B]$ | 0.90(4)                  | 0.68(4)                  | 0.72(3)                  | 0.68(3)                  |
| $\mu_{TB}(Ti^{3+}) [\mu_B]$ | 0.22(1)                  | 0.17(1)                  | 0.18(1)                  | 0.17(1)                  |
| $\mu_{TB}(Ti^{3+}) [\mu_B]$ | 0.61(2)                  | 0.46(2)                  | 0.56(2)                  | 0.52(2)                  |
| $\mu_{TB}(Ti^{3+}) [\mu_B]$ | 2.27(4)                  | 2.39(3)                  | 2.23(3)                  | 2.48(3)                  |
| $\mu_{TB}(Ti^{3+}) [\mu_B]$ | 0.57(1)                  | 0.60(1)                  | 0.56(1)                  | 0.62(1)                  |
| $\mu_{TB}(Ti^{3+}) [\mu_B]$ | 1.55(2)                  | 1.64(2)                  | 1.72(2)                  | 1.90(2)                  |
| $\mu_{TB}(Ti^{3+}) [\mu_B]$ | 0.019 / 0.041            | 0.007 / 0.042            | 0.023 / 0.041            | 0.012 / 0.052            |
| $\mu_{TB}(Ti^{3+}) [\mu_B]$ | 0.25(10)                 | 0.15(8)                  | 0.31(8)                  | 0.55(7)                  |
| $M [\mu_B]$ | 0.32                      | 0.32                      | 0.35                      | 0.35                      |
| $\mu_{TB}(Ti^{3+}) [\mu_B]$ | 0.96                      | 0.96                      | 0.96                      | 0.96                      |
| $\mu_{TB}(Ti^{3+}) [\mu_B]$ | 3.84                      | 3.84                      | 3.84                      | 3.84                      |
| $\mu_{TB}(Co^{3+}) [\mu_B]$ | 0.75(5)                  | 0.80(4)                  | 0.60(4)                  | 0.65(3)                  |

$\eta$ gives the contribution of the Lorentzian part. In figure 6 it can be seen that the Lorentzian part for $Ti_{0.8}Mn_{0.2}Co_{2}O_{4}$ is strongly increasing with the temperature reaching finally a pure Lorentzian peak shape at about 90 K somewhat below the magnetic ordering temperature $T_{m} = 112$ K. In contrast, for $Ti_{0.6}Mn_{0.4}Co_{2}O_{4}$ the pure Lorentzian peak shape is already reached at 10 K below the compensation point. As reported earlier a pure Lorentzian peak shape has been observed for $TiCo_{2}O_{4}$ in the full temperature range which was found to be broadened [20]. The change of the peak shape can be ascribed to the presence of a superimposed contribution of diffuse scattering. But it has to be mentioned that a Lorentzian peak shape may also describe the distribution of the magnetic mosaic blocks or the presence of short-range order frozen in a spin-glass state. Further studies are needed to give a detailed quantitative description of this behaviour. According to the chemical percolation approach reported by Cowley et al one should expect Bragg scattering occurs from the largely linked clusters, together with a diffuse scattering occurring from the limited ferrimagnetic clusters below a critical composition [44]. In such case the correlation length should consist of two components, (i) transverse component which diverges across $T_{m}$ and decreases below and it is associated with critical fluctuations within the infinite cluster. The second one is the (ii) longitudinal component which dominates at low temperature and it is linked to the finite clusters. It is well known that diffuse scattering is an important tool for analyzing such longitudinal and transverse spin components, in particular, the short-range-order of reentrant spin-glass systems in which the disordered reenters at low-temperature below $T_{m}$.

In the present case a slight decrease of the A-site magnetic moment indicates the coexistence of longitudinal and transverse spin components associated with a long-range ordered magnetic
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The long-range ordering temperature revealing the presence of diffuse scattering superimposed on the reflection 200. Such well-resolved Bragg reflections, originating from the spatial ordering of the transverse-spin components (TSC), indicates the presence of canted local spin configuration on the $B$ sublattice (similar to the Yafet–Kittel’s (Y-K) three sublattice model) [19, 45, 52]. Usually, in a non-collinear system, the individual site moments deduced from the neutron diffraction study are due to the longitudinal spin components of the canted site moments, whereas the transverse components do not contribute to the normal Bragg reflections. In a triangular spin-lattice Bragg reflections arise due to the spatial ordering of the transverse spin components. Thus, the origin of the Bragg reflection 200 indicates the presence of a canted local spin configuration on the $B$ sublattice. These results are consistent with the previous reports [45, 52]. We have evaluated the canting angle ($\alpha_{Y,K}$) using the individual $B$-site moments (AF and FI) derived from the neutron diffraction study of $\text{Ti}_{1-x}\text{Mn}_x\text{Co}_2\text{O}_4$ with $x = 0.2$ and $x = 0.4$. Accordingly, the canting angle $\alpha_{Y,K}$ lies between $66.9$ and $73.7^\circ$ for $x = 0.2$, and $71$ and $74.1^\circ$ for $x = 0.4$. Such non-collinear behavior of spins causes substantial decrease of the magnitude of $B$-sublattice moments than the expected value and frequency dispersion of the dynamic susceptibility (which will be discussed in later sections). Usually, the transverse spin-glass component (often called ‘semi-spin-glass’) coexists with the longitudinal-spin component when the magnetic ions are diluted with non-magnetic ions like Ti$^{4+}$, Sn$^{4+}$ or Zn$^{2+}$. Because of such dilution and magnetic frustration the spins in the $B$ sublattice may cant locally [53]. Theoretical studies reported by Villain show that two distinct transitions may occurs in such semi-spin glass systems. The first one is the Néel temperature $T_N$ corresponding to the breakdown of LSC and the second transition is the spin-glass freezing temperature $T_F$ at which the TSC freezes-in [53].

3.3. Electronic structure

The electronic and chemical state of the elements in $\text{Ti}_{1-x}\text{Mn}_x\text{Co}_2\text{O}_4$ polycrystalline samples was analyzed by

![Figure 5](image1.png)

Figure 5. Temperature dependence of the ferrimagnetic moments of the ions in (a) $\text{Ti}_{0.8}\text{Mn}_{0.2}\text{Co}_2\text{O}_4$, and (b) $\text{Ti}_{0.6}\text{Mn}_{0.4}\text{Co}_2\text{O}_4$ located at the $A$ and $B$ sites. The $A$ site is only occupied with Co$^{3+}$ ions (labelled as $\text{Co}_A$), while the $B$ site contains Ti$^{3+}$, Mn$^{3+}$ and Co$^{3+}$ (labelled as $\text{Ti}_B$). For the $B$ site only the averaged moments are given. The bold lines are a guide for the eye.

![Figure 6](image2.png)

Figure 6. Change of the peak shape of the magnetic reflection (1 0 1) with increasing Mn content. A pure Lorentzian peak shape has been observed for $\text{TiCo}_2\text{O}_4$, where one also finds a broad diffuse signal giving an uneven background. The data of $\text{TiCo}_2\text{O}_4$ were taken from our earlier study [20]. With increasing Mn content a reduction of diffuse scattering is observed. The strong increase of the magnetic intensity of the reflection (1 0 1)$_K$ can be ascribed to the fact that the magnetic moment of Mn is much stronger than that of Ti. An increase of the Mn content also leads to change of the peak shape, where the Lorentzian part $\eta$ of the pseudo-Voigt function is decreasing. The pseudo-Voigt function is defined as $pV(x) = \eta L(x) + (1 - \eta) G(x)$. Interestingly the Lorentzian part $\eta$ is also increasing as a function of temperature shown in the lower part of the figure. From the instrumental resolution curve one expects at the position of the reflection (1 0 1)$_K$ a FWHM of 0.52° which practically has a Gaussian shape. The bold line is a guide for the eye.
meets the O-1 s core level photoelectrons whose photoelectron intensity was plotted as a function of binding energy (eV). All these spectra were calibrated by selecting the binding energy of carbon C-1 s orbital (located at E_C = 284.8 eV) as an internal reference. The Mn-2p spectrum of octahedrally coordinated ‘Mn’ ion in Ti_{0.6}Mn_{0.4}Co_{2}O_{4} spinel is shown in figure 8(a) which requires a minimum of three peaks (two main peaks at 640.45 eV and 652.12 eV, and one broad satellite peak at 628.52 eV) to reproduce the spectrum. The peak component of Mn is constrained to have the same peak profile within the binding energy range of 0.2 eV. The binding-energy separation between the Mn doublet ∆E_{Mn}(E_{p1/2} – E_{p3/2}) ∼ 11.67 eV signifies the trivalent oxidation state of Mn inside the core of spinel structure Ti_{1-x}Mn_{x}Co_{2}O_{4} [54–56]. The observed value of ∆E_{Mn} in the present investigating system is slightly higher (∼0.46 eV) as compared to undoped MnCo_{2}O_{4} [55]. Such higher value of ∆E_{Mn} is associated with the increase in the screening strength of Mn^{3+} ion by the additional Ti^{3+} ion present in the Ti_{1-x}Mn_{x}Co_{2}O_{4} matrix.

The core level XPS spectrum of Co-2p consist of two doublets of Co(II) (at 794.6 eV) and Co(III) (779.3 eV) together with three broad satellite peaks (as shown in figure 8(b)) positioned at 783.4, 789.9 and 804.1 eV. For the peak fitting, we have imposed a constraint that the ratio between the areas of the Co-2p_{3/2} and Co-2p_{1/2} for Co(II) and Co(III) should be same. This constrain is relaxed at the final step of the peak fitting. From the fitting analysis, we have calculated the spin–orbit splitting energy (∆E) between the doublets ∆E_{Co^{3+}}(2p_{3/2} – 2p_{1/2}) and ∆E_{Co^{2+}}(2p_{3/2} – 2p_{1/2}), which comes out to be 15.3 and 15.78 eV, respectively, signifying the two different oxidation states of Co (trivalent and divalent states) [20, 57].

On the other hand, Ti-2p core level spectrum (figure 8(c)) is deconvoluted into two major peaks (doublet) located at 457.44 and 463.01 eV, together with two high-energy shake up satellite peaks centered at 470.46 and 475.04 eV. The initial fitting parameters are obtained from the NIST XPS Database [58]. The intensity ratio of the Ti-2p_{3/2} and Ti-2p_{1/2} peaks is also constrained to 2:1 ratio [58]. The Ti-2p_{1/2} peak profile is slightly broader (∼0.28 eV) than the Ti-2p_{3/2} peak due to the Coster–Kronig effect [59]. The magnitude of spin–orbit splitting ∆E_{Ti}, between the Ti-2p_{3/2} and Ti-2p_{1/2} (∼5.58 eV) signifies the presence of trivalent electronic state of Ti inside Ti_{0.6}Mn_{0.4}Co_{2}O_{4} [59]. In order to confirm the Ti^{3+} oxidation state, we have carried out a systematic correlation between the Ti-O bond length (obtained from the Rietveld refinement data) and a robust parameter ∆O-Ti i.e. the binding energy difference between the O-1s and Ti-2p_{3/2} [60]. The experimentally observed value of ∆O-Ti ∼ 72.6 and the Ti-O bond length ∼2.058 Å confirm the presence of Ti^{3+} oxidation state. Had Ti existed in tetravalent oxidation state, the values of ∆O-Ti and Ti-O bond length would lie in the range 71 eV ≤ ∆O-Ti ≤ 72 eV and 1.94 Å ≤ Ti-O ≤ 1.97 Å, respectively [60]. For divalent oxidation state of Ti the aforementioned parameters would be ∆O-Ti ∼ 75 eV with Ti-O bond length ∼2.08 Å.

Finally, the O-1s spectrum is deconvoluted into two partially resolved Gaussian-Lorentzian peaks centered at 530.03 and 528.88 eV as shown by arrow marks in figure 8(d). The main origin of highest intensity peak at 528.88 eV is associated with the bonding between metal and lattice oxygen (Mn-O, Ti-O and Co-O), while the low intensity peak at 530.03 eV is associated with the surface-adsorbed oxygen [57]. The asymmetric behavior observed in O-1s core level spectrum is mainly associated with the presence of oxygen vacancies and different atomic environment faced by the O^{2–} anions [61].

### 3.4. Thermal variation of magnetic-susceptibilities and specific-heat

In this section we present the temperature variation of dc-magnetic susceptibilities χ(T) of both Ti_{0.6}Mn_{0.4}Co_{2}O_{4} (figure 9) and Ti_{0.8}Mn_{0.2}Co_{2}O_{4} (figure 10) measured under ZFC and field-cooled (FC) conditions. We have performed these measurements in the presence of different external dc-magnetic fields H_{dc} between 500 Oe and 50 kOe, however, figures 9 and 10 show the variation of χ(T) at H_{dc} = 500 Oe (figures 9(a) and 10(a)) and 50 kOe (figures 9(b) and 10(b)) for Ti_{0.6}Mn_{0.4}Co_{2}O_{4} and Ti_{0.8}Mn_{0.2}Co_{2}O_{4}, respectively. For Ti_{0.6}Mn_{0.4}Co_{2}O_{4} the χ(T) curves show ferrimagnetic behavior
with a giant bifurcation ($\Delta \chi \sim 7.74 \times 10^{-3}$ emu/gOe) between the $\chi_{ZFC}(T)$ and $\chi_{FC}(T)$ due to very high magnetocrystalline anisotropy. The ferrimagnetic ordering is suggested to result from unequal/opposite magnetic moments of cations occupied at the tetrahedral A site [$\mu_{\downarrow}(\text{Co}^{2+})$] and the octahedral B site [$\mu_{\uparrow}(\text{Mn}^{3+}, \text{Ti}^{3+} \text{and} \text{Co}^{3+})$].

For the composition, Ti$_{0.6}$Mn$_{0.4}$Co$_2$O$_4$ both $\chi_{ZFC}(T)$ and $\chi_{FC}(T)$ exhibit peaks at 104.1 K ($T_{p-ZFC}$) and 60 K ($T_{p-FC}$), and drops to zero across the $T_C \sim 110.3$ K. It is interesting to note that $\chi_{ZFC}(T)$ exhibits negative values for all the temperatures below 96 K with a negative maximum ($-2.32 \times 10^{-3}$ emu/gOe) at 56.1 K, while the magnitude of $\chi_{FC}$ decreases significantly below $T_{p-FC}$ without any negative values. Such markedly different characteristics of $\chi_{FC}(T)$ and $\chi_{ZFC}(T)$ below their peak values (at $T_{p-ZFC}$ and $T_{p-FC}$) are mainly due to the different temperature dependence of the magnetic moments associated with the cations occupying A and B sites. For the accurate determination of the ordering temperature we have determined the susceptibility derivatives (based on the Fisher’s relation [62]). Accordingly, we have plotted the temperature dependence of the product $\chi T$ (left hand side scale) and its derivative $d(\chi T)/dT$ (right hand side scale) in the insets of figures 9(a) and 10(a). Interestingly we noticed two peaks $T_{P1}$ and $T_{P2}$ in the $d(\chi T)/dT$ plotted as a function of temperature. The peak position $T_{P1}$ is close to 110.27 K for 500 Oe signifying the exact value of $T_C$ (consistent with hump noticed at 109.1 K from $C_p$ versus $T$ and $C_p T^{-1}$ plots shown in figure 11), whereas for the high fields (50 kOe) much broader $T_{P1}$ (115.3 K) and $T_{P2}$ (50.7 K) are noticed.

On the other hand, a remarkable change in the $\chi(T)$ behavior was observed with decreasing Ti$^{3+}$-ion concentration at the B site of the spinel lattice. Magnetic compensation effect at 25.4 K ($T_{COMP}$), negative magnetization in $M_{FC}$ below $T_{COMP}$ and drastic decrease in $T_C$ (82 K) from ($\chi - T$) plot for $H_{dc} = 500$ Oe are the noteworthy features observed for $x = 0.2$ system (figure 10). It is well known that magnetic compensation occurs in systems where the two sublattices magnetization balances with each other (similar to Co$_2$TiO$_4$, $T_{COMP} = 30.4$ K) [20]. Below the compensation point ($T_{COMP}$) an opposite trend was observed between $\chi_{FC}$ (−ve values) and $\chi_{ZFC}$ (+ve values). For $x = 0.2$, both $\chi_{FC}(T)$ and $\chi_{ZFC}(T)$ exhibits cusp like behavior with the peak positions at 72.1 (500 Oe) and 64 K (50 kOe) corresponding to the maximum susceptibility values $\chi_{Max}(T_{P-ZFC}) = 3.42 \times 10^{-3}$ emu/gOe and $\chi_{Max}(T_{P-FC}) = 4.07 \times 10^{-3}$ emu/gOe, respectively. Without any Mn contribution (i.e. for $x = 0$ case Co$_2$TiO$_4$ system) the
The applied field for compensation phenomena at $T_{\text{COMP}} = 25.4$ K, represented by a blue arrow mark in the main panel. However, such consonance with the neutron experiments gradually decreases to zero in the presence of external dc-magnetic field $H_{\text{dc}}$, whereas the dc-magnetization experiments were performed in zero-field condition. The red color solid line represents the lattice contribution of specific heat calculated from numerical fits using equation $C_{P\text{-Lattice}} = Nf_D(\Theta_D/T) = 9 N R (T/\Theta_D)^3 \int_0^{\Theta_D} \frac{x^4 e^x}{(e^x - 1)^2} \, dx$ as described in the text and green solid circular symbols represent the magnetic contribution to the specific heat. The R.H.S scale shows the temperature dependence of $C_{P\text{-Total}}$ showing the transition at 109.1 K clearly.
for $T \gg T_C$ where the effect of magnetic contribution is expected to be negligible [64]. Such fitting analysis yields $\Theta_0 = 488.7$ K for Ti$_{0.6}$Mn$_{0.4}$Co$_2$O$_4$ polycrystalline sample which is 37 K lower than the $\Theta_D$ of antiferromagnetic Co$_3$O$_4$ and 72 K lower than the $\Theta_D$ of ferrimagnetic TiCo$_2$O$_4$ [9, 65]. The extrapolated data is shown in figure 11 together with the contribution of the $C_{P,\text{Lattice}}$ and $C_{P,\text{Magnetic}}$ components obtained from the above analysis [63]. For $T < 47.8$ K the contribution from $C_{P,\text{Magnetic}}$ starts dominating over $C_{P,\text{Lattice}}$ due to the freezing down of phonons and the reorientation of spins in preferred directions. It is interesting to note that $C_{P,\text{Magnetic}}$ remains constant (13 J/mol K) between 62 and 108 K. The absence of a sharp peak in the $C_P(T)$ motivated us to perform the dynamic response of the magnetic susceptibility and its temperature and frequency dependent characteristics with the aim to probe the degree of disorderness and the existence of spin-glass nature in these systems. Figure 12 shows the temperature dependence of real and imaginary components of the ac-magnetic susceptibility $\chi_{ac}(f, T) = \chi'(f, T) + i\chi''(f, T)$ recorded at constant driving frequency 51 Hz and peak-to-peak amplitude of the ac-magnetic field $h_{ac} \sim 4$ Oe for different dc-bias-fields ($0 \leq H_{dc} \leq 300$ Oe) superimposed with $h_{ac}$. Both the in-phase and out-of-phase susceptibility curves exhibit cusp like behavior with significant decreases in the peak position ($T_P$) and intensity as $H_{dc}$ increases. For $x = 0.4$ (0.2), $T_P$ shifts from 110.7 K (78.22 K) to 102.4 K (71 K) for $H_{dc}$ increases from 0 to 300 Oe. The inset of figure 12(b) shows the variation of $T_P$ as a function of $H_{dc}^{1/3}$ which shows a straight-line behavior consistent with the de Almeida–Thouless line (AT-line) $[H_{AT}(T_P) = A_{AT} (1 - T_P/\Theta_0)^\alpha]$ [66–68]. Analysis, usually adopted to probe the spin-glass like magnetic disordered state in variety of compounds. Here AT-line defines the onset of a transition from the frozen spin-glass like state to reversible magnetic behavior at the peak temperature in $\chi_{ac}(f, T)$ under zero dc-field. It is interesting to note that the in-phase susceptibility cusp splits into two peaks with increasing the magnitude of $H_{dc}$ (figure not shown). The extent of peak splitting increases with increasing $H_{dc}$ whereas for the out of phase susceptibility $\chi''$, only a single cusp was noticed which decreases in amplitude and shifts to lower temperatures with increasing $H_{dc}$. The AT-line criteria are often used in the literature to study the characteristic features of spin-glass ordering in amorphous magnets and magnetic ultrafine particles [68–70]. The linear behavior of the plot $T_P$ versus $H_{dc}^{1/3}$ for low applied fields confirms the AT-like phase boundary where the linear extrapolation of AT-line on the temperature axis, in the limit $H_{dc}$ approaches to zero yields the freezing temperature $T_F$ (i.e. $T_F(0) \sim 78.15$ and 110.5 K for $x = 0.2$ and 0.4, respectively). Such AT-line crossover in the $H-T$ plane has been reported for a variety of spin-glass compounds such as CuMn [71], AgMn [72], AuFe [73], Fe$_x$Mn$_{1-x}$TiO$_3$ [74] etc. However, determination of the freezing temperature using the AT-line criteria as a standard proof is not enough to probe the spin-glass behavior, instead empirical scaling laws are needed [75–78]. Therefore, in order to probe the existence of exact spin-glass nature in the current system we performed a detailed frequency dependent study. Figure 13 shows the temperature variation of $\chi'$ and $\chi''$ measured at various frequencies between 0.17 Hz and 1.2 kHz under heating condition without any superimposition of $H_{dc}$ with $h_{ac} \sim 4$ Oe for both the compositions. One can clearly notice a shift in the maximum point of the cusp towards high temperature side with increasing the frequency for both the systems, however, for $x = 0.4$ this shift is more significant than the lower composition $x = 0.2$. Usually, such dispersion in the peak position signifies the spin-disorderness (glassyness) in the system. In order to confirm the existence of such spin-randomness (spin-glass nature) we used two empirical scaling laws: (i) the Vogel–Fulcher-law (VFL) $\tau = \tau_0 \exp \left( E_J/k_B(T_f - T_0) \right)$ for interacting particle systems, and (ii) the power-law (PL) $\tau = \tau_0 \left( T_f / T_0 \right)^{-\nu}$ describing the critical slowing down [77, 78]. In the above expressions, the parameter $\tau_0$ represents the relaxation time constant, $T_0$ is a measure of the interparticle interaction strength on
magnetic relaxation, $k_B$ is the Boltzmann constant, $E_a$ is an activation energy parameter, $\nu$ is a critical exponent and $T_F$ is the spin-glass freezing temperature. Figure 13(e) shows the logarithmic variation of the relaxation time ($\tau$) as a function of $\ln(T - T_F)/T_F$. The scattered points represent the variation of the peak temperature ($T_P$) determined from $\chi'(T)$ for both the compositions. The solid continuous lines connecting the experimental data points represent the best fit to the PL. On the other hand, figure 13(f) shows the variation of $1/\ln(\tau/\tau_0)$ versus $T_F$ related to the VFL described above. Here $\tau_0$ values obtained from the PL have been used to fit the experimental data points for VFL. In both the cases (VFL and PL) we

| Table 3. The list of various fitting parameters obtained from straight line fitting of ac-susceptibility data using the VFL and PL. |
|---|---|---|
| Sample | Parameters corresponding to PL | Parameters corresponding to VFL | $\nu$ values from $\ln(\frac{\tau}{\tau_0}) \sim \frac{E_a}{k_B(T - T_F)}$ |
| | $\tau = \tau_0 \left( \frac{T}{T_F} - 1 \right)^{-\nu}$ | $\tau = \tau_0 \exp\left( \frac{E_a}{k_B(T - T_0)} \right)$ | 
| $\text{Ti}_0.8\text{Mn}_{0.2}\text{Co}_2\text{O}_4$ | Using $\chi'(f,T)$ | Using $\chi'(f,T)$ | 4.37 |
| | $\tau_0 = 1.48 \times 10^{-14}$ s | $\tau_0 = 1.48 \times 10^{-14}$ s | |
| | $T_F = 78.1 \pm 0.02$ K | $E_a = 10.3 k_B$ | |
| | $\nu = 4.22 \pm 0.01$ | $T_0 = 77.82 \pm 0.02$ K | |
| | $\text{Ti}_0.6\text{Mn}_{0.4}\text{Co}_2\text{O}_4$ | Using $\chi''(f,T)$ | Using $\chi''(f,T)$ | 4.9 |
| | $\tau_0 = 3.67 \times 10^{-15}$ s | $\tau_0 = 3.67 \times 10^{-15}$ s | |
| | $T_F = 78.03 \pm 0.02$ K | $E_a = 20.82 k_B$ | |
| | $\nu = 4.6 \pm 0.02$ | $T_0 = 77.46 \pm 0.01$ K | |
| | $\text{Ti}_0.8\text{Mn}_{0.2}\text{Co}_2\text{O}_4$ | Using $\chi'(f,T)$ | Using $\chi'(f,T)$ | 5.18 |
| | $\tau_0 = 1.6 \times 10^{-15}$ s | $\tau_0 = 1.6 \times 10^{-15}$ s | |
| | $T_F = 110.1 \pm 0.02$ K | $E_a = 32.0 k_B$ | |
| | $\nu = 5.23 \pm 0.01$ | $T_0 = 109.56 \pm 0.02$ K | |
| | $\text{Ti}_0.8\text{Mn}_{0.4}\text{Co}_2\text{O}_4$ | Using $\chi''(f,T)$ | Using $\chi''(f,T)$ | 5.94 |
| | $\tau_0 = 3.48 \times 10^{-14}$ s | $\tau_0 = 3.48 \times 10^{-14}$ s | |
| | $T_F = 109.99 \pm 0.02$ K | $E_a = 48.87 k_B$ | |
| | $\nu = 5.38 \pm 0.03$ | $T_0 = 108.82 \pm 0.02$ K | |
obtained the straight line behavior with different fitting parameters which are listed in table 3. The following fitting parameters are evaluated from PL for \( x = 0.2(0.4) \): \( T_0 = 1.48 \times 10^{-14} \) s \((1.6 \times 10^{-15})\), \( T_E = 78.1 \) K \((110.32 \) K) and \( z
u = 4.22 \) (5.23) using the frequency variation of \( \chi(T) \). Alternatively, using the VFL we obtained for \( x = 0.2(0.4) \): \( E_a = 10.3 \) kJ \((32.02 \) kJ), and \( T_0 = 77.82 \) K \((109.56 \) K). Using the fitting parameters obtained from VFL and the relation between the VFL and PL (i.e. \( \ln \left( \frac{400T_E}{E_a} \right) \sim \frac{25}{\nu} \)) [67], we have reevaluated the magnitudes of \( z
u \) which are in excellent agreement with the values determined from PL (table 3). In general, typical spin-glass system exhibit ‘\( \tau_o \)’ values between \( 10^{-9} \) and \( 10^{-16} \) s and the \( z
u \) values between 4 and 12 [67, 77]. The \( \tau_o \) and \( z
u \) values for \( \text{Ti}_{0.8}\text{Mn}_{0.2}\text{Co}_2\text{O}_4 \) and \( \text{Ti}_{0.8}\text{Mn}_{0.2}\text{Co}_2\text{O}_4 \) lies within the above specified range for spin glasses. Thus the investigated compounds exhibit a spin-glass state just below the ferrimagnetic ordering due to the Mn substitution in \( \text{TiCo}_2\text{O}_4 \) (often called as reentrant spin-glass state).

### 3.5. Magnetic hysteresis and remanence

Figure 14 shows the magnetization versus field \((M-H)\) hysteresis loops of \( \text{Ti}_{0.8}\text{Mn}_{0.2}\text{Co}_2\text{O}_4 \) and \( \text{Ti}_{0.8}\text{Mn}_{0.2}\text{Co}_2\text{O}_4 \) measured between -50 kOe to +50 kOe at selected temperatures below \( T_C \) after 50 kOe field cooling. The temperature of the sample was raised to 300 K \((\gg T_C)\) before the \( M-H \) measurement to ensure perfect paramagnetic state to avoid any remanence field in the samples. All the hysteresis loops are unsaturated even up to 50 kOe and the magnetization increases linearly with field. Also, the spontaneous magnetization per formula unit is slightly larger than the magnitude of magnetic moments determined from the neutron diffraction and the linear contribution represents the non-collinear arrangement of spins. The angle of the spins usually changes due to the torque exerted by the magnetic field, thus leading to a linear increase in the magnetization value with increasing the field within the magnetically ordered state. The hysteresis loops of \( \text{Ti}_{0.6}\text{Mn}_{0.4}\text{Co}_2\text{O}_4 \) exhibit giant coercivity \((H_C \sim 26.3 \) kOe at 5 K) and loop asymmetry (loop-shift popularly known as exchange-bias, \( H_{EB} \sim -10.6 \) kOe at 5 K) due to very high magnetocrystalline anisotropy dominant at low temperature. The magnitude of \( H_C \) and \( H_{EB} \) are estimated using the relations \( H_C = (H^+ - H^-)/2 \), and \( H_{EB} = (H^+ + H^-)/2 \), where the quantities \( H^+ \) and \( H^- \) are the magnetic field values at which magnetization becomes zero. Both \( H_C \) and \( H_{EB} \) decrease gradually as the temperature approaches \( T_C \). We also observed that a weak ferrimagnetic component \( M_{WF} \) is essentially superimposed on a linear AF component in the ordered state. The temperature variation of both \( H_C \) and \( H_{EB} \) are shown in figures 15 (i) and (iii) for the compositions \( x = 0.2 \) and 0.4, respectively. At \( T = 5 \) K, the \( H_C \) value of \( \text{Ti}_{0.8}\text{Mn}_{0.2}\text{Co}_2\text{O}_4 \) reaches a maximum of 26.3 kOe which gradually decreases to 4.6 kOe at 60 K. On the other hand, \( H_{EB} \) reaches a minimum value of \(-10.6 \) kOe at 5 K and a sign reversal occurs at 9.7 K finally reaches a maximum value of +0.6 kOe at 10 K. Beyond 10 K, \( H_{EB} \) gradually deceases and approaches to zero. For the composition \( \text{Ti}_{0.8}\text{Mn}_{0.2}\text{Co}_2\text{O}_4 \), no significant coercivity or remanence was noticed in the \( M-H \) loops recorded below 5 K, but as the temperature increases loops open-up and exhibits significant \( H_C \) and \( M_{R} \) values for \( T > 5 \) K. The magnitude of \( H_C \) gradually increases with increasing the temperature \((H_C \sim 0.98 \) kOe at 5 K) and reaches its maximum value of 9.4 kOe at 40 K and drops to 0.44 kOe at 70 K. While a crossover from +3.7 kOe to \(-1.3 \) kOe was noticed in the \( H_{EB} \) values when the temperature increases from 5 to 25 K, respectively. Such polarity change in the exchange bias is also associated with the highly frustrated magnetic spins and negative magnetization behavior. For \( T > 25 \) K, the \( H_{EB} \) decreases and gradually approaches to zero as \( T \rightarrow T_C \). Similarly, we have evaluated the remanence magnetization \( M_R \) value at \( H = 0 \) and the maximum magnetization \( M_{MAX} \) at 50 kOe for both the samples whose temperature dependence is shown in figures 15 (ii) and (iv). Interestingly, both \( M_R \) and \( M_{MAX} \) increase progressively with the rise of temperature for \( x = 0.2 \) and 0.4. The maximum \( M_R = 4.58 \) emu/g and 1.9 emu/g was observed for \( x = 0.2 \) and 0.4, respectively. A clear anomaly in \( M_R(T) \) was noticed across 15 K for \( x = 0.2 \) which is consistent with the field induced transition noticed in \( \chi(T) \) (figure 10(b)) and \( M_R \) decreases slightly across the \( T_{COMP} \) for this system.
4. Conclusions

The structural, electronic and magnetic properties of two different compositions of a B-site substituted Ti$_{1-x}$Mn$_x$Co$_2$O$_4$ system have been investigated in detail by neutron diffraction, x-ray photoelectron spectroscopy (XPS), specific-heat, static and dynamic magnetization measurements. Based on the evidence gathered from the dc-magnetization data and ac-susceptibility we have specifically chosen two compositions $x = 0.2$ and 0.4 for a detailed neutron diffraction study because these two systems exhibit evidence for the negative magnetization, magnetic compensation effect, reentrant spin-glass behavior and exchange-bias effect. The refinements of the crystal structure in the space group I4$_1$/amd provides the evidence of a weak tetragonal distortion with $c/a < 1$ for the compositions $x = 0.2$ and 0.4, respectively. Due to the dimness of this distortion the presence of a Jahn–Teller effect is not really supported by these data. However, the refinements in the tetragonal structure give rise to weak changes of the apical and equatorial bond lengths. These changes are compatible with the trend which is expected for a Jahn–Teller activity of the Mn$^{3+}$ ions having the 3d$^4$ configuration. The elemental analysis performed by XPS confirms the presence of trivalent state of all the octahedrally coordinated B-site cations (Ti(3d$^1$), Mn(3d$^4$) and Co(3d$^6$)) and divalent electronic state of tetrahedrally coordinated A site Co which are in-line with the neutron diffraction and magnetization data. Our neutron diffraction study clearly shows the diffuse neutron scattering from 200 reflections which indicate the presence of canted local spin configuration (Yafet–Kittel like ordering) due to the transverse spin component at low-temperatures. Observation of the diffuse scattering and variation in canting angle with the Mn substitution are the most significant features of the current investigated system. Neutron diffraction studies also confirm the presence of a strong ferrimagnetic (FI) coupling between the magnetic A- and B-site ions below $T_C = 110.3$ K (for $x = 0.4$) and 78.2 K (for $x = 0.2$). Furthermore, an additional weak antiferromagnetic (AF) component was found lying perpendicular to the FI component. Although the moment directions of AF and FI components could not be determined, it is possible to determine the spin sequence of the AF ordering in which the moments were assumed to be aligned parallel with or perpendicular to the $c$ axis. Thermal variation of the individual and net magnetic moments $\mu_{FI}(TB)$, $\mu_{FI}(CoA)$, ($TB$ being the cations at B sites) obtained from neutron diffraction agree more or less with the temperature dependence of the dc-magnetic susceptibility $\chi(T)$ data. However, the moments $\mu_{FI}(CoA)$ and $\mu_{FI}(TB)$ gradually decrease to zero in consonance with the $\chi(T)$, but could not see any negative moment or any anomaly across the compensation point ($\sim$ 25.4 K for $x = 0.2$) which were observed in the $\chi(T)$ data. This discrepancy is due to the fact that the neutron diffraction measurements were performed under zero-field case, whereas the dc-magnetization experiments were performed in the presence of a strong dc-field. The current neutron diffraction results demonstrate that the unequal growth of magnetic moments in the cations at tetrahedral A and octahedral B sites, and their different temperature dependence

Figure 15. Temperature dependence of coercive field $H_C$ and the exchange bias field $H_{EB}$ ((i), (iii)). The remanence magnetization $|M_R|$ and high field (50 kOe) magnetization $|M_{MAX}|$ ((ii), (iv)) of Ti$_{0.6}$Mn$_{0.4}$Co$_2$O$_4$ and Ti$_{0.8}$Mn$_{0.2}$Co$_2$O$_4$ are also shown.
plays a significant role in realizing the magnetization reversal for all the compositions \( x \leq 0.2 \). Interestingly as compared to the parent compound TiCO\(_2\)O\(_4\), the Ti\(_{0.6}\)Mn\(_{0.4}\)CO\(_2\)O\(_4\) sample exhibits a giant coercive field \( H_c \approx 26 \) kOe, and negative exchange bias \( H_{EB} \approx -10.6 \) kOe at low temperatures which vanishes as the measuring temperature approaches towards \( T_C \). From the temperature dependence of the total specific-heat \( C_{P,\text{Total}}(T) \) we have evaluated the individual contributions of lattice and magnetic components. Accordingly, we have determined the Debye temperature \( \Theta_D = 488.7 \) K (for Ti\(_{0.6}\)Mn\(_{0.4}\)CO\(_2\)O\(_4\)) which is significantly lower (by 65.5 K) than the \( \Theta_D \) value of single crystal TiCO\(_2\)O\(_4\). The frequency and temperature dependence of the dynamic-susceptibility \( \chi_{ac}(f, T) \) data follows the AT-line criterion in the \( T-H \) plane and empirical scaling laws (i.e. Vogel – Fulcher-law and power-law) for both the compositions \( x = 0.2 \) and \( x = 0.4 \) suggesting the spin-glass like ordering below \( T_g \approx 78.1 \) and 110.1 K with critical exponents \( \nu = 4.22 \) and 5.23, and relaxation time constant \( \tau_0 = 1.48 \times 10^{-14} \) and \( 1.6 \times 10^{-15} \) s.

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References

[1] Nii Y, Sagayama H, Umetsu H, Abe N, Taniguchi K and Arima T 2013 Phys. Rev. B 87 195115
[2] Lee K H, Chang H, Hwang I Y, Chung J H, Kang H W, Kim S J and Lee S 2015 Phys. Rev. B 91 064404
[3] Tanaka T and Ishihara S 2009 Phys. Rev. B 79 035109
[4] Ohtani S, Watanabe Y, Saito M, Abe N, Taniguchi K, Sagayama H, Arima T, Watanabe M and Noda Y 2010 J. Phys.: Condens. Matter 22 176003
[5] Reeves M, Tovar M, Tobbens D, Pattison P, Hosier A and Lake B 2015 Phys. Rev. B 91 024407
[6] Guillou F, Thota S, Prellier W, Kumar J and Hardy V 2011 Phys. Rev. B 83 094423
[7] Hoshi T, Katori H A, Kosaka M and Takagi H 2007 J. Magn. Magn. Mater. 310 e448–50
[8] Srinivasan G and Seehra M S 1983 Phys. Rev. B 28 1
[9] Roth W 1964 J. Phys. Chem. Solids 25 1–10
[10] Tomiyasu K, Ueda H, Matsuda M, Yokoyama M, Iwasa K and Yamada K 2011 Phys. Rev. B 84 035115
[11] Suzuki T and Katsufuji T 2009 J. Phys. Conf. Ser. 150 042195
[12] Melot B C, Drewes J E, Seshadri R, Stoudenmire E and Ramirez A P 2009 J. Phys.: Condens. Matter 21 216007
[13] Kemei M C, Moffitt S L, Shoemaker D P and Seshadri R 2012 J. Phys.: Condens. Matter 24 046003
[14] Tackett R, Lawes G, Melot B C, Grossman M, Toberer E S and Seshadri R 2007 Phys. Rev. B 76 024409
[15] Suzuki T and Katsufuji T 2008 Phys. Rev. B 77 220402
[16] Hirai S, dos Santos A M, Shapiro M C, Molaison J J, Fradhan N, Guthrie M, Tulk C A, Fisher I R and Mao W L 2013 Phys. Rev. B 87 014417
[17] Kim C, Jo E, Kang B, Kwon S, Lee S, Shim J H, Suzuki T and Katsufuji T 2012 Phys. Rev. B 86 224420
[18] Padam R, Pandya S, Ravi S, Nigam A, Ramakrishnan S, Grover A and Pal D 2013 Appl. Phys. Lett. 102 112412
[19] Hubsch J and Gavoille G 1982 Phys. Rev. B 26 3815
[20] Thota S et al 2017 Phys. Rev. B 96 144404
[21] Zhang H, Wang Z, Liu E, Wang W, Yue M and Wu G 2015 J. Appl. Phys. 117 17B735
[22] Kalikowski J and Lesniewski A 1980 J. Magn. Magn. Mater. 19 117–9
[23] Carey M, Maat S, Rice P, Farrow R, Marks R, Kellok A, Nguyen P and Gurney B 2002 Appl. Phys. Lett. 87 1044–6
[24] Jiang C, Wu L, Wei W, Dong C and Yao J 2014 Nanoscale Res. Lett. 9 584
[25] Hu W, Qin N, Wu G, Lin Y, Li S and Bao D 2012 J. Am. Chem. Soc. 134 14658–61
[26] Kreizho T and Konstantinov P 1992 J. Phys.: Condens. Matter 4 L543
[27] Thota S and Searpha M 2013 J. Appl. Phys. 113 203905
[28] Mandrus D, Keppens V and Chakoumakos B 1999 Mater. Res. Bull. 34 1013–22
[29] Li C, Yan T, Chakrabarti C, Zhang R, Chen X, Fu Q, Yuan S and Barasa G O 2018 J. Phys. Appl. Phys. 123 093902
[30] Fu C, Li G, Luo D, Huang X, Zheng J and Li L 2014 ACS Appl. Mater. Interfaces 6 2439–49
[31] Molin S, Jasinski P, Mikkelsen L, Zhang W, Chen M and Hendriksen P V 2016 J. Power Sources 336 408–18
[32] Yang Z, Xia G, Simmer S P and Stevenson J W 2005 J. Electrochem. Soc. 152 A1896–901
[33] Boucher B, Buhl R, Di Bella R and Perrin M 1970 J. Physique 31 113–9
[34] Granroth G, Mandrus D, Keppens V and Nagler S 2004 J. Magn. Magn. Mater. 272 1306–7
[35] Mondal A K, Su D, Chen S, Ung A, Kim H S and Wang G 2015 Chem. – Eur. J. 21 1526–32
[36] Li L et al 2014 Electrochim. Acta 116 467–74
[37] Yuvaraj S, Vignesh H R, Vaseylehco L, Lee Y and Selvan K R 2016 RSC Adv. 6 69016–26
[38] Arrebola J, Caballero A, Hernán L and Morales J 2008 J. Nanomater. 2008 16
[39] Srivastava J, Kalikarni J, Ramakrishnan S, Singh S, Marathe V, Chandra G, Darshane V and Vijayaramagavan R 1987 J. Phys. C: Solid State Phys. 20 2139
[40] Rodríguez-Carvajal J 1993 Physica B 192 55–69
[41] Sears V F 1995 International Tables for Crystallography vol C (Dordrecht: Kluwer)
[42] Brown P J 1995 International Tables for Crystallography vol C (Dordrecht: Kluwer)
[43] Joy P and Date S 2000 J. Magn. Magn. Mater. 210 31–4
[44] Cowley R A, Shirane G, Birgeneau R J and Guggenheim H J 1977 Phys. Rev. B 15 4292
[45] Chakrarthy R, Rao L M, Paranjpe S, Kulshreshtha S and Roy S 1991 Phys. Rev. B 43 6031
[46] Yoshizawa H, Mitsuwa S, Aruga H and Ito A 1987 Phys. Rev. Lett. 59 2364
[47] Wong P Z, Von Molnar S, Palstra T, Mydosh J, Yoshizawa H, Shapiro S and Ito A 1985 Phys. Rev. Lett. 55 2043
[48] Kleemann W, Shvartsman V, Borisov P and Kania A 2010 Phys. Rev. Lett. 105 257202
[49] Frantz G, Schmidt M and Zimmer F 2019 *Physica* A **516** 464–71
[50] Kmjec T et al 2019 *J. Magn. Magn. Mater.* **475** 334–44
[51] Ghara S and Sundaresan A 2018 *J. Phys.: Condens. Matter* **30** 245802
[52] Murthy N S, Natera M, Youssef S, Begum R and Srivastava C 1969 *Phys. Rev.* **181** 969
[53] Villain J 1979 *Z. Phys.* B **33** 31–42
[54] Kim K J and Heo J W 2012 *J. Korean Phys. Soc.* **60** 1376–80
[55] Pramanik P, Thota S, Singh S, Joshi D C, Weise B, Waske A and Seehra M 2017 *J. Phys.: Condens. Matter* **29** 425803
[56] Wei H, Ma J, Li B, An L, Kong J, Yu P and Xia D 2016 NPG Asia Mater. **8** e255
[57] Kim J G, Pugmire D, Battaglia D and Langell M 2000 *Appl. Surf. Sci.* **165** 70–84
[58] Naumkin A V, Kraut-Vass A, Gaarenstroom S W and Powell C J 2000 NIST X-Ray Photoelectron Spectroscopy Database (NIST Standard Reference Database 20, Version 4.1) (Gaithersburg MD: National Institute of Standards and Technology) p 20899
[59] Biesinger M C, Lau L W, Gerson A R and Smart R S C 2010 *Appl. Surf. Sci.* **257** 887–98
[60] Atuchin V V, Kesler V G, Pervukhina N V and Zhang Z 2006 *J. Electron Spectrosc. Relat. Phenom.* **152** 18–24
[61] Aswaghosh L, Manoharan D and Jaya N V 2016 *Phys. Chem. Chem. Phys.* **18** 5995–6004
[62] Fisher M E 1962 *Phil. Mag.* **7** 1731–43
[63] Bouvier M, Lethuillier P and Schmitt D 1991 *Phys. Rev.* B **43** 13137
[64] Gopal E 1966 *Specific Heats at Low Temperatures* (International Cryogenics Monograph Series) (New York: Plenum) (https://doi.org/10.1007/978-1-4684-9081-7)
[65] Ogawa S and Waki S 1965 *J. Phys. Soc. Japan* **20** 540–5
[66] De Almeida J and Thouless D J 1978 *J. Phys. A: Math. Gen.* **11** 983
[67] Souletie J and Tholence J 1985 *Phys. Rev.* B **32** 516
[68] Nakamura S, Soeya S, Ikeda N and Tanaka M 1993 *J. Appl. Phys.* **74** 5652–7
[69] Mukadam M, Yusuf S, Sharma P, Kulshreshtha S and Dey G 2005 *Phys. Rev.* B **72** 174408
[70] Singh M K, Katiyar R S, Prellier W and Scott J 2008 *J. Phys.: Condens. Matter* **21** 042202
[71] Djurberg C, Jonason K and Nordblad P 1999 *Eur. Phys. J.* B **10** 15–21
[72] Bouchiat H and Monod P 1986 *J. Magn. Magn. Mater.* **54** 124–6
[73] Taniguchi T and Miyako Y 1988 *J. Phys. Soc. Japan* **57** 3520–31
[74] Katori H A and Ito A 1993 *J. Phys. Soc. Japan* **62** 4488–502
[75] Shtrikman S and Wohlforth E 1981 *Phys. Lett.* A **85** 467–70
[76] Binder K and Young A P 1986 *Rev. Mod. Phys.* **58** 801
[77] Mydosh J A 1993 *Spin Glasses: An Experimental Introduction* (Boca Raton, FL: CRC Press)
[78] Tholence J 1980 *Solid State Commun.* **35** 113–7