Structure and magnetism of the β-Mn–Co solid-solution phase

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1. Introduction

Manganese stands out among the metallic elements with its unique crystal structures and odd magnetic properties. The trend-breaking features are associated with the α- and β-modifications of Mn whereas the properties of the high-temperature (γ and δ) or -pressure (ε) variants largely comply with the pattern traced out along the 3d series. The immediate impression of the crystal structures of α- and β-Mn is that, these phases have more in common with intermetallic compounds than pure elements. This impression is further reinforced by the fact that many proper binary and quaternary intermetallics take the α- and β-Mn-type structural arrangements [1]. Our interest in this complex element arose through the finding that the low-temperature Au80−xSn20 phase is isostructural with β-Mn [2].

Despite frequent studies from 1925 [3,4] onward (the crystal structures of α- and β-Mn were in all essentials solved in 1927–1928 [5,6]) more well-grounded insight into the structural and magnetic properties, phase stability, phase transitions, etc. for the various polymorphs of Mn has only been attained rather recently. Ab initio spin-density-functional computational studies [7,8] have shown that the complex crystal and magnetic structures of α- and β-Mn are the results of the conflicting desires to maximize simultaneously bond strength and magnetic moment. Frustration of antiferromagnetic (AF) exchange interactions leads to a non-collinear arrangement of the moments in α-Mn and a quantum spin-liquid state in β-Mn. Simple AF ground states are found for γ- and δ-Mn whereas the computational results suggest that ε-Mn should be only marginally magnetic at equilibrium. All in all it appears (see the very thorough survey of experimental and theoretical findings in Refs. [7,8]) that the structural and magnetic phase diagram of Mn is well explained by the density-functional approach. However, there are still open questions in relation to the various polymorphs of Mn.

One could expect the following consequences of the substitution of Mn by Co in β-Mn. (i) The spin configuration degeneracy will be removed, resulting in relief of the magnetic frustration. (ii) Replacement of Mn by Co is equivalent to addition of extra electrons to the lattice. If the electron concentration plays an important role in the adoption of the unusual crystal structure and magnetic properties, this can be understood. (iii) Substitution of Mn by a

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non-magnetic element, e.g., Al slows down the strong AF-correlated spin fluctuations (see, e.g., Refs. [9,10] and references therein) and shifts such systems toward conventional co-operative magnetism. Replacement of Mn by another magnetic atom such as Co may also facilitate long-range magnetic ordering.

The present paper is focused on the structural and magnetic properties of the β-Mn–Co solid-solution phase. Our working hypothesis was that extensive substitution of Co for Mn might release the magnetic frustration and allow deeper exploration of the co-operative magnetic state. However, we were already at the start of the project aware that the spin-liquid state of pure β-Mn probably extends to at least β-Mn0.75Co0.25 [11]. On the other hand, the homogeneity range of quenched β-Mn1−xCox extends right out to x ≈ 0.43 [12,13].

We report here on a magnetic susceptibility and powder neutron-diffraction (PND) investigation of β-Mn1−xCox (0 ≤ x ≤ 0.40). Because PND experiences a methodological problem (see Section 3) near to t = 0.25, structural data for t = 0.0, and 0.40 were also collected with single-crystal X-ray diffraction (SXD).

For evaluation of the structural findings it is convenient to regard the co-operative magnetic state. However, we were already at the start of the project aware that the spin-liquid state of pure β-Mn probably extends to at least β-Mn0.75Co0.25 [11]. On the other hand, the homogeneity range of quenched β-Mn1−xCox extends right out to x ≈ 0.43 [12,13].

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2. Experimental

Samples with nominal compositions Mn, Mn0.85Co0.15, Mn0.75Co0.25, and Mn0.60Co0.40 (hereafter rounded off to t = 0.15, 0.25, and 0.40) were collected with single-crystal X-ray diffraction (SXD). For evaluation of the structural findings it is convenient to regard the SXD-based redefined structure of β-Mn by Shoemaker et al. [14] as a bench-mark standard.

After the initial treatment all samples were carefully crushed and transferred to new silica-glass capsules (evacuated and sealed) and annealed at 1000°C for 7 days. The heat treatment of the cobalt-containing samples were conducted by controlled cooling from 1000 to 500°C over days (7 days for some of the samples of Mn0.60Co0.40) and then quenched to room temperature.

The refinements of the SXD data were terminated at quite acceptable values for the first few parameters of interest.

The PND diagrams of β-Mn at 298 and 12 K immediately established lack of conventional co-operative magnetism down to the latter temperature, thus confirming PND findings reported already in 1956 by Kasper and Roberts [21] and later confirmed in various studies (see, e.g., Refs. [8,9,11,22–25] and references therein). The negative findings indeed ruled out the possibility of ‘more exotic co-operative arrangements like heli-, cone-, and fan-magnetism’ which we hinted at in Ref. [2]. This part of the exercise was of course superficial, as the literature is unanimous on the lack of conventional co-operative magnetic ordering in β-Mn, but we evidently had a desired personal confirmation. The virtually temperature-independent magnetic susceptibility of β-Mn below 298 K (Fig. 2) is in conformity with the absence of conventional co-operative magnetism, again in accordance with earlier findings [9,22–25].

The PND for data β-Mn0.75Co0.25 and β-Mn0.60Co0.40 match those for t = 0 with regard to lacking evidences for conventional co-operative magnetism. However, in line with the findings for with a SMART CCD diffractometer (Siemens) equipped with an Oxford Cryosystems Cryostream Plus device. Mo Kα radiation (71.073 pm) was used and the range of θ covered was 4.58 to 59.64–61.36° (depending on specimen), limiting indices being −15 ≤ h ≤ 15 and −14 ≤ k ≤ 14 for h, and l [ca. 17.000 reflections collected (internal R in the range 0.051–0.066), 631–671 of which being independent]. The data were integrated with SMART [18], corrected for absorption with SADABS [19], and refined using full-matrix least squares against F(H) with SHELXL [20]. Anisotropic displacement parameters were taken into account and an unequal degree of substitution on the two sites was allowed in the initial refinements of the structures for t = 0.25 and 0.40. Based on these findings all Co was fixed at the Tl site in the final refinements of β-Mn0.75Co0.25. The number of parameters/restrictions was accordingly 10/0 in the final refinements of the structures for t = 0 and 0.25 and 14/4 for t = 0.40. The refinements of the SXD data were terminated at satisfactory values for the reliability factors (R1 = 0.0196–0.0401, wR2 = 0.0546–0.0880, Goof = 1.222–1.328).

Magnetic susceptibility measurements were carried out between 4 and 300 K in a field of 1 kOe using a SQUID magnetometer (Magnetic Property Measurement System, Quantum Design). Data were collected on heating with 30–40 mg samples contained in gelatin holders during the measurements.

3. Results

Unit-cell dimension (a) for the present β-Mn1−xCox samples are listed in Table 1, and isotherms showing the compositional variation of a at 10/12, 150, and 298 K are shown in Fig. 1. Fig. 1 also includes corresponding room-temperature data available from the literature [13,14], the mutual consistency of which with the present findings being quite good. This is gratifying since the results quoted from the compilation of Pearson [13] refer to chemically analyzed samples. Hence, the close match in Fig. 1 serves to support the use of the nominal compositions as representative measures for the actual compositions of the present samples.

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![Fig. 1](image-url)
Table 1: Unit-cell dimensions and positional parameters for the \( \beta\)-Mn\(_{1-x}\)Co\(_x\) phase (space group \( \text{P}4_1\text{c}2\); \( T_1\) in position 8c, \( T_2\) in position 12d) with e.s.d in parenthesis.

<table>
<thead>
<tr>
<th>( t )</th>
<th>( T ) (K)</th>
<th>( a ) (pm)</th>
<th>( x ) for ( T_1 )</th>
<th>( y ) for ( T_2 )</th>
<th>Occupancy of ( T_1 )</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>298</td>
<td>631.5 (2)</td>
<td>0.0636 (1)</td>
<td>0.2022 (1)</td>
<td>Mn</td>
<td>SXD</td>
</tr>
<tr>
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<td>298</td>
<td>631.59 (6)</td>
<td>0.0668 (3)</td>
<td>0.2009 (3)</td>
<td>Mn</td>
<td>PND</td>
</tr>
<tr>
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<td>150</td>
<td>629.9 (2)</td>
<td>0.0624 (1)</td>
<td>0.2019 (1)</td>
<td>Mn</td>
<td>SXD</td>
</tr>
<tr>
<td>0.00</td>
<td>12</td>
<td>627.47 (6)</td>
<td>0.0650 (3)</td>
<td>0.1989 (3)</td>
<td>Mn</td>
<td>PND</td>
</tr>
<tr>
<td>0.15</td>
<td>298</td>
<td>632.19 (2)</td>
<td>0.0659 (6)</td>
<td>0.2022 (2)</td>
<td>0.625 Mn + 0.375 Co</td>
<td>PND</td>
</tr>
<tr>
<td>0.25</td>
<td>298</td>
<td>632.04 (5)</td>
<td>0.0630 (5)</td>
<td>0.2027 (3)</td>
<td>0.375 Mn + 0.625 Co</td>
<td>PND</td>
</tr>
<tr>
<td>0.25</td>
<td>150</td>
<td>630.6 (2)</td>
<td>0.06293 (8)</td>
<td>0.20184 (8)</td>
<td>0.375 Mn + 0.625 Co</td>
<td>SXD</td>
</tr>
<tr>
<td>0.40</td>
<td>298</td>
<td>628.4 (2)</td>
<td>0.015 (9)</td>
<td>0.1991 (7)</td>
<td>0.375 Mn + 0.625 Co</td>
<td>PND</td>
</tr>
<tr>
<td>0.40</td>
<td>150</td>
<td>629.44 (2)</td>
<td>0.0634 (5)</td>
<td>0.2009 (2)</td>
<td>0.19 Mn + 0.81 Co</td>
<td>SXD</td>
</tr>
<tr>
<td>0.40</td>
<td>150</td>
<td>625.98 (2)</td>
<td>0.06197 (3)</td>
<td>0.2012 (2)</td>
<td>0.22 Mn + 0.78 Co</td>
<td>SXD</td>
</tr>
<tr>
<td>0.40</td>
<td>10</td>
<td>625.98 (2)</td>
<td>0.0640 (5)</td>
<td>0.2093 (2)</td>
<td>0.20 Mn + 0.80 Co</td>
<td>SXD</td>
</tr>
<tr>
<td>0.40</td>
<td>298</td>
<td>628.82 (3)</td>
<td>0.0631 (5)</td>
<td>0.2024 (3)</td>
<td>0.12 Mn + 0.88 Co</td>
<td>PND</td>
</tr>
</tbody>
</table>

\( a \) See also Fig. 1.
\( b \) “Ideal” parameter values; \( x = 1/(9 + \sqrt{33}) \approx 0.0678 \), \( y = (9 - \sqrt{33})/16 \approx 0.2035 \), see text.
\( c \) The powder samples contained some 3% MnO which was corrected prior to the structure refinement.
\( d \) Nominal compositions, see text.
\( e \) Data quoted from Ref. [14].
\( f \) Essentially identical values for \( a, x, \) and \( y \) were obtained for the large and smaller crystals; see Section 2.
\( g \) Fixed, all Co restrained to the \( T_1 \) site.
\( h \) Data quoted from Ref. [14].
\( i \) Methodologically induced error, see text.
\( j \) Fixed at values complying with the PND findings.
\( k \) The powder samples contained some 3% MnO which was corrected prior to the structure refinement.
\( l \) Essentially identical values for \( a, x, \) and \( y \) were obtained for the large and smaller crystals; see Section 2.
\( m \) Sample quenched from 900 °C.
\( n \) PND.

\( T_\text{d} \) Nominal compositions, see text.

The variable parameters of the \( \beta\)-Mn\(_{1-x}\)Co\(_x\) phase were subjected to Rietveld refinements of the PND data for all samples. All together ten different refinement models were tested, including the alternative space groups \( \text{P}4_1\text{c}2\) and \( \text{P}2_1\text{c}3 \) and various assumptions concerning the distribution of Mn and Co over the involved sites. Owing to the different sign of the neutron scattering length of Mn and Co, PND is a very sensitive tool to discriminate between distribution alternatives in this case. The conclusions from the Rietveld analyses were that no significant improvements in reliability factors were obtained on turning to the lower symmetric space group and [except for the most substituted \( t = 0.40 \) sample] nearly all Co was found to have entered position 8c of space group \( \text{P}4_1\text{c}2\). The final positional and occupancy parameters are listed in Table 1 and corresponding interatomic distances are given in Table 2. In relation to the PND data for \( t = 0.25 \) it should be noted that average scattering length for 3 Mn and 5 Co randomly distributed over position 8c is unfavourably small (\( b = 0.339 \) fm). This methodological complication is reflected in the unreasonable values obtained for the \( x \) parameter for this sample at 10 and 298 K, whereas the occupancy parameter for the 8c site still can be accurately assessed (Table 1). In order to remedy this defect it was searched for a suitable single crystal of \( \beta\)-Mn\(_{0.75}\)Co\(_{0.25}\) for SXD examination. Such a specimen was indeed found and the subsequent search for single crystals of \( \beta\)-Mn and \( \beta\)-Mn\(_{0.60}\)Co\(_{0.40}\) was also successful. SXD data for these specimens (see Section 2) were collected at 150 K and the refinement of which gave the parameter values for \( x \) and \( y \) included in Table 1. Note that the positional parameters could be quite precisely determined from SXD data whereas occupancy parameters are less sensitive to the distribution of Co between the two sites. In the final refinement cycles the latter parameters were accordingly fixed at values complying with the PND findings.

4. Discussion

If the solutes in phases with \( \beta\)-Mn-type structure exclusively enter the 8c site, there would occur a natural phase limit at 40% substitution of Co for Mn. Hence, the pronounced site preference of Co for site 8c rationalizes why the \( \beta\)-Mn\(_{1-x}\)Co solid-solution range only extends up to \( t = 0.43 \) [11,12,13]. However, this in turn releases a number of related questions, some of which being formulated and addressed below.

Among the 3d series of \( \beta\)-Mn\(_{1-x}\)T\(_1\) phases those with a T element following Mn (viz. \( T = \text{Fe–Zn} \)) show more extended solid-solution ranges than those with \( T = \text{Sc–Cr} \) [11,12,13]. What
Table 2

<table>
<thead>
<tr>
<th>Composition</th>
<th>0</th>
<th>0.15</th>
<th>0.25</th>
<th>0.40</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1–T2</td>
<td>234.7</td>
<td>236.4</td>
<td>235.1</td>
<td>236.3</td>
</tr>
<tr>
<td>T1–T2</td>
<td>236.0</td>
<td>257.6</td>
<td>259.6</td>
<td>257.9</td>
</tr>
<tr>
<td>T2–T1</td>
<td>268.7</td>
<td>268.0</td>
<td>267.1</td>
<td>265.6</td>
</tr>
<tr>
<td>T2–T1</td>
<td>268.0</td>
<td>257.6</td>
<td>259.6</td>
<td>257.9</td>
</tr>
<tr>
<td>T2–T2</td>
<td>268.0</td>
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<td>259.6</td>
<td>257.9</td>
</tr>
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<td>268.0</td>
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<td>T2–T2</td>
<td>268.0</td>
<td>257.6</td>
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</tr>
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<td>T2–T2</td>
<td>268.0</td>
<td>257.6</td>
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<td>257.9</td>
</tr>
<tr>
<td>T2–T2</td>
<td>268.0</td>
<td>257.6</td>
<td>259.6</td>
<td>257.9</td>
</tr>
</tbody>
</table>

**Notes:**

a. Assuming a = 0.6315 pm from Ref. [14].
b. Based on structural parameters from Ref. [14].
c. Interatomic distances which involve T1 are burdened with methodological problem (see text).
d. Sample quenched from 900°C.
e. Method.

Table 2

<table>
<thead>
<tr>
<th>Composition</th>
<th>0.15</th>
<th>0.25</th>
<th>0.40</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1–T2</td>
<td>268.0</td>
<td>268.0</td>
<td>267.1</td>
</tr>
<tr>
<td>T1–T2</td>
<td>268.0</td>
<td>268.0</td>
<td>267.1</td>
</tr>
<tr>
<td>T2–T1</td>
<td>268.0</td>
<td>268.0</td>
<td>268.0</td>
</tr>
<tr>
<td>T2–T1</td>
<td>268.0</td>
<td>268.0</td>
<td>268.0</td>
</tr>
</tbody>
</table>

A characteristic feature of the composition variation in the unit cell of the Mn–Co–Fe (Fig. 1) is that a(t) goes through a flat maximum somewhere between t = 0.10 and 0.25. The initial increase in the a(t) isotherms can be rationalized by accepting that Co has a somewhat larger size than the Mn1 host it replaces (see Fig. 6 in Ref. [2]). The composition dependence of the averages for the 12 Mn1–Mn and 14 Mn2–Mn bond distances at 298, 150, and 10 K (Table 2) lends support to such an inference. (Note that the averages are less infested with random errors than the individual distances.)

What could then cause a(t) to decrease again? One feature which clearly comes into the picture is the dispersing of the substituting Co atoms on the 8c site as well as the larger sized 12d site. The actual observations for 8c Mn–Co (see Table 1) suggest that the observed change in the occupancy pattern between the two sites could be a significant contributing factor to the more rapid decline of a(t) toward t = 0.40. In general, a(t) is determined by not only the distribution of Mn and Co between the T1 and T2 sites but also by the short- and long-range orders within the two sites. In this connection we draw attention to the composition variation of the long-range order parameter for the corresponding 12–Mn1–Fe phase deduced from 57Fe Mössbauer spectroscopy [28]. This study shows that with increasing Fe content, the long-range-order parameter for the Fe distribution follows a dependence which somewhat resembles a(t) in Fig. 1.

Another characteristic feature, which the Mn–Co–Fe phase has in common with isostructural phases, is the comparative constancy of the positional parameters x and y and their closeness rather than full conformity to the “ideal” (see Refs. [2,29]) values for these parameters. As evident from Table 2 there is indeed some variation in the bonding interatomic distances with composition and temperature. The overall trend is that the bond distances are shortest at the highest substitution level (t = 0.40) and lowest temperature (10 K).

A detailed comparison of the bond distances corresponding to the “ideal” [2,29] values of x and y with those actually observed for the Mn–Co–Fe phase (Table 2) leads to the conclusion that there is not a geometric (viz. symmetry) factor which prevents the structure from accepting the “ideal” demands. This finding appears to be a logical consequence of the somewhat unspecific constraint which crops up in the formulation of the ideality criterion [2,29]: as many as possible of the shorter T1–T2 distances are required to be equal and similarly for the six shortest T1–T2 distances.

The recent comprehensive density-functional theoretical exploration of allotropes of manganese [7,8] concluded that the complex crystal structure and frustrated magnetism of Mn–Co are the results of conflicting desires to maximize simultaneously bond strength and magnetic moment. The computational efforts moreover established that the ambient pressure polymorphs α, β, γ, and δ are close in energy which inter alia has allowed the many studies of Mn as a metastable phase at and below room temperature. That is all very well, but it is more interesting to trace features which make the Mn–Co type structure with its differently sized Mn atoms so favourable. We intend to pursue this problem by theoretical examination of the chemical bonding in Mn–Co phases.

Given the Mn–Co structural arrangement the lacking conventional co-operative magnetism of Mn–Co might at first be regarded as a trivial prolongation of the geometrically frustrated situation of the magnetic moments at t = 0. However, the introduction of Co into the picture has altered two magnetic distinguishing marks compared to the pristine phase. (i) The diffuse scattering of magnetic origin which appears in the PND diagrams...
for \( t > 0 \) has no counterpart for \( t = 0 \). (ii) The virtually temperature
independent paramagnetic susceptibility characteristic for pure \( /H_9252-Mn \) develops into a more and more Curie–Weiss-like relationship
for \( t > 0 \). These tendencies indicate that magnetic traits of char-
acter become enhanced on the Co-for-Mn substitution. However,
the non-observation of long-range magnetic ordering shows that
the spin-configurational degeneracy is not removed by the Co-for-
Mn substitution. This implies that the magnetic frustration arising
from the corner-shared triangular sub-units created by Mn2 are not
appreciably affected by the Co substitution. This is consistent with
the experimental fact that Co predominantly prefers to occupy the
Mn1 site, and could in turn provide another reason for why the sol-
ubility of Co in \( /H_9252-Mn \) is limited to \( \sim 40 \) at\%. On the other hand, if
one accepts the postulated [8] decisive role of regular Mn1Mn3
13
tetrahedra for the structure and other properties of \( /H_9252-Mn \) as a re-
ference frame, the frustration would then rather be consequence
of the perturbation of the majority Mn2 atoms by the intruded
Co atoms on the Mn1 sublattice. According to this picture long-
range magnetic ordering facilitated by Co substitution breaks the
tetrahedral units and hence lifts the degeneracy of the spin config-
uration. As the frustration of the spins arising from corner-shared
Mn2 triangles should not be influenced noticeably by Co-for-Mn
substitution, the long-range magnetic ordering would remain sup-
pressed.

We have for the time being no plausible explanation(s) to offer
for the gradually more and more Curie–Weiss-like relationship
for \( t > 0 \) (note with unphysically large paramagnetic moments and
Weiss constants), but we intend to pursue also these features by
computational density-functional means.

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