Study of the ferromagnetic quantum phase transition in Ce$_{3-x}$Mg$_x$Co$_9$

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ABSTRACT
The Ce$_{3-x}$Mg$_x$Co$_9$ system evolves from a Pauli paramagnetic ground state for $x=0$ to a ferromagnetic ground state for $x \approx 0.80$ in single-phase, polycrystalline samples [Lamichhane, V. Taufour, A. Palasyuk, Q. Lin, S.L. Budko, and P.C. Canfield, Ce$_{3-x}$Mg$_x$Co$_9$: transformation of a Pauli paramagnet into a strong permanent magnet, Phys. Rev. Appl. 9 (2018), p. 024023]. In order to better understand this behaviour, single-crystalline samples of Ce$_{3-x}$Mg$_x$Co$_9$ for $x = 0.01$, $0.16$, $0.24$, $0.35$, $0.43$ and $0.50$ were grown using the flux growth technique, and electrical transport and magnetic properties were studied. The $T_C$-$x$ phase diagram we infer shows that the system has a quantum phase transition near $x = 0.35$, transforming to a ferromagnetic ground state.

KEYWORDS
Pauli paramagnet; quantum phase transition; ferromagnet

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1. Introduction

Fragile magnetism is the study of nearly degenerated magnetic ground states at low temperature which can be tuned with non-thermal parameters such as pressure, chemical substitution and external fields. Fragile magnetic systems [1] tuned via chemical substitution can lead to quantum criticality, or more generally, a second-order quantum phase transition at 0 K [2]. There are several examples of quantum critical points in heavy fermions systems in which magnetic impurity doping induces second-order quantum phase transition at 0 K such as CeCd$_{6-x}$Au$_x$, YbRh$_2$(Si$_{0.95}$Ge$_{0.05}$)$_2$ and other variants in rare-earth elements and Si, Ge concentrations [2]. There are also some examples of transition metal-based compounds showing the nonthermal parameters chemical substitution driven quantum phase transitions such as Pd$_{1-x}$Ni$_x$ [3] and Cr$_{1-x}$V$_x$ [4]. Here we investigate a Pauli paramagnetic to ferromagnetic quantum phase transition in Ce$_{3-x}$Mg$_x$Co$_9$ [5, 6].
Despite being 75% atomic Co, pure CeCo$_3$ has a Pauli paramagnetic, low-temperature ground state. In polycrystalline samples of Ce$_{3-x}$Mg$_x$Co$_9$, structural and transformation of a Pauli paramagnetic CeCo$_3$ into a ferromagnetic phase was studied in our earlier work [5]. It is a rhombohedral crystal system with space group $R\bar{3}m$. There are two inequivalent Ce-sites among where 3$g$ sites are partially substituted with Mg. Though the systematic experimental investigation is not done, our speculation of development of itinerant ferromagnetism via tuning the density of states of Co-bands [5] agrees with first-principle calculations [6]. A similar example of doping-induced quantum phase transition of a Pauli paramagnetic to ferromagnetic system is observed in a lightly Fe-doped (Cr$_{1-x}$Fe$_x$)$_2$B system [7]. This system exhibits a quantum phase transition along with a distinct intermediate antiferromagnetic phase and associated non-Fermi liquid behaviours in thermodynamical and transport properties. However, in this study, no intermediate phase and non-Fermi liquid behaviour was not observed in the studied physical properties. For single-phase samples, ferromagnetism was observed for $x \geq 0.80$. In mixed-phase samples, signs of magnetic order could be found for $x < 0.80$, but in such samples, magnetism could be influenced by several factors such as defects [8], stress [9], impurities [10], etc. To elucidate the phase transformation in a much cleaner way, the study of magnetism using single-phase, single-crystalline samples is always a better idea. We investigated the magnetic properties, electrical transport and specific heat capacity of selected compositions around $x \approx 0.35$ of single-crystalline Ce$_{3-x}$Mg$_x$Co$_9$ samples.

We find a quantum phase transition as Ce$_{3-x}$Mg$_x$Co$_9$ changes from a Pauli paramagnetic state for $0 \leq x < 0.35$ to a ferromagnetic state for $0.35 < x < 1.4$. No additional magnetic phases were found in the vicinity of the quantum phase transition composition.

2. Experimental details

Single crystalline Ce$_{3-x}$Mg$_x$Co$_9$ samples for $x \leq 0.5$ were synthesised in 3-cap Ta crucibles [11] similar to the previous report [5] by maintaining the Ce+Mg to Co ratio as 30:70, i.e. (Ce$_{1-x}$Mg$_x$)$_{30}$Co$_{70}$ with nominal $x = 0.05$, 0.10, 0.15, 0.20, 0.25 and 0.30 as listed in Table 1.

The selected amount of Ce–Co–Mg elements were sealed under almost one atmospheric pressure of Ar at room temperature inside a 3-cap Ta crucible. The Ta crucibles were protected under a partial pressure of Ar inside an amorphous silica jacket with quartz wool buffers on the top and the bottom of the crucible to protect silica ampoule from the consequences of differential thermal expansion during temperature ramping and mechanical shock during the decanting process. The silica ampoule was heated to 900°C over 3 h and held there for 3 h to allow the initial reaction of elements and potentially avoid the excessive boiling of Mg at a higher temperature. Then the growth
was heated to 1200°C over 3 h and held there for 10 h to form a homogeneous liquid. Finally, the growth was slowly cooled down to 1040°C over \(\sim 100\) h for nominal Mg content \(x = 0.05 - 0.15\) and centrifuged to separate the crystals from the flux. Similarly, growths with \(x = 0.20 - 0.30\) were cooled down to 1070°C over \(\sim 100\) h and crystals were separated. The single-crystalline samples had rhombohedral plate-like morphology with several millimetres in length and width and approximately 1–2 mm in thickness. The easy axis of magnetisation is perpendicular to the plate ([001] direction) [5].

Crystals from all the batches were characterised using powder X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). For XRD, a finely ground powder was spread over the zero background silicon wafer and held in place with a thin film of Dow Corning high vacuum grease. Powder XRD data were collected using Rigaku Miniflex II diffractometer within 2\(\theta\) range of 5–100° using a step size of 0.01° and a dwell time of 3 s. For SEM, single crystalline samples were mounted in epoxy and finely polished perpendicular to the plane of the plate to determine the composition. The nominal composition, average Energy Dispersive Spectroscopy (EDS) composition, and Rietveld refined composition are presented in Table 1. For nominal Mg \(x = 0.05, 0.10\) and 0.15 samples, traces of CeCo\(_2\) impurities were visible in the cross-sectional view of SEM images (not shown here). The EDS and Rietveld refined composition more or less agree with each other except for nominal 5% Mg-doped sample. Hereafter, all the compositions are EDS inferred in this paper.

Magnetic properties were measured in a Quantum Design (QD) Magnetic Property Measurement System (MPMS) in between 2 and 300 K. A QD Versa-Lab Vibrating Sample Magnetometer (VSM) was used to measure the magnetic properties between 50 and 400 K. All the magnetisation data were measured with a magnetic field parallel to [001] direction. The internal magnetisation field \(H_{int}\) was determined as \(H_{int} = H_{applied} - N \times M\) to determine the Curie temperature using Arrott plots [12]. Here, \(N\) is the demagnetisation factor related to sample geometry and \(M\) is the magnetisation. The details of the demagnetisation factors determination can be found elsewhere [13–15]. Electrical transport property was measured using the four-probe method with a Linear

| Loaded nominal composition | EDS composition | Rietveld refined composition |
|----------------------------|----------------|-----------------------------|
| Ce\(_{29}\)Co\(_{71}\)     | Ce\(_{2.99}\)Co\(_{0.01}\) | Ce\(_{2.95}\)Co\(_{0.05}\) |
| Ce\(_{28}\)Mg\(_{2}\)Co\(_{70}\) | Ce\(_{2.98}\)Co\(_{0.02}\) | Ce\(_{2.87}\)Co\(_{0.13}\) |
| Ce\(_{25}\)Mg\(_{4}\)Co\(_{70}\) | Ce\(_{2.76}\)Co\(_{0.24}\) | Ce\(_{2.75}\)Co\(_{0.25}\) |
| Ce\(_{22}\)Mg\(_{6}\)Co\(_{70}\) | Ce\(_{2.53}\)Co\(_{0.37}\) | Ce\(_{2.57}\)Co\(_{0.43}\) |
| Ce\(_{21}\)Mg\(_{8}\)Co\(_{70}\) | Ce\(_{2.50}\)Co\(_{0.50}\) | Ce\(_{2.49}\)Co\(_{0.51}\) |

Notes: The uncertainty in Mg content is given in parentheses which was obtained as a standard deviation of EDS measurement. The average uncertainty in Mg concentration in the Rietveld refinement is \(\pm 0.05\).
research Inc. meter bridge LR 700 (1 mA; 17 Hz excitation). Thin platinum wires were attached to the resistance bar using DuPont 4929N silver paint to make electrical contacts. An MPMS was used as a temperature controller for the electrical transport measurements. The specific heat capacity was measured in a QD physical property measurement system using the relaxation technique.

3. Results and discussion

Ce$_{3-x}$Mg$_x$Co$_9$ forms in the rhombohedral (space group $R$–3$m$) structure for all $x$ examined [5, 16]. Figure 1 shows the variation of the lattice parameters $a$ and $c$ with Mg content. The $c$ lattice parameter decreases monotonically, whereas the $a$ lattice parameter is more or less constant up to $x \leq 0.50$.

Figure 2 shows the zero-field cooled (ZFC) temperature-dependent magnetisation $M(T)$ for $x \leq 0.50$. Although CeCo$_3$ was identified as a Pauli paramagnetic compound long ago [17], there has been some room for the question because of the presence of a low-temperature upturn in temperature-dependent magnetisation [5]. Moreover, recent density functional calculation showed CeCo$_3$ could order ferromagnetically at low temperature [6]. With $x \leq 0.24$ of Mg addition, the low-temperature magnetisation remains temperature independent and manifests Pauli paramagnetism as shown in the inset of Figure 2. These temperature independent magnetisation data for $x = 0.01$, 0.16, and 0.24 confirm that for these $x$-values, Ce$_{3-x}$Mg$_x$Co$_9$ is Pauli paramagnetic system. Since $x = 0.01$ sample is Pauli paramagnetic down to 2 K, this suggests that pure CeCo$_3$ may also be a Pauli paramagnetic. The low temperature upturn [5] is most likely associated with magnetism of impurity ions or traces of extrinsic magnetic impurity.

**Figure 1.** Variation of lattice parameters of Ce$_{3-x}$Mg$_x$Co$_9$ with Mg content $x$ inferred from EDS. The uncertainty of the lattice parameters values is less than 0.2%. The dashed lines are guides to the eye.
As we increase the value of $x$, a low temperature upturn starts to become visible for $x = 0.35$ suggesting it may be close to a critical concentration for achieving the quantum phase transition. For $x = 0.43$ and 0.50, the upturns in $M(T)$ data upon cooling develop large enough magnetisation to suggest that they are ferromagnetic samples. The kink only visible on the ZFC $M(T)$ data for $x = 0.43$ and 0.50 could be related to the reorientation of ferromagnetic domains near the transition temperature.

To better understand the evolution of ferromagnetism with Mg content $x$, a detailed analysis of easy axis $M(H)$ data was performed for all samples. Figure 3 shows the 2 K $M(H)$ data for the non-ferromagnetic samples with

![Figure 3](image)

**Figure 2.** ZFC temperature dependent magnetisation $M(T)$ data of various $\text{Ce}_{3-x}\text{Mg}_x\text{Co}_9$ samples at 300 Oe applied field. The inset shows the enlargement around the upturns to highlight the ferromagnetism development with higher concentrations of Mg.

![Figure 3](image)

**Figure 3.** Field-dependent magnetisation of various non-ferromagnetic $\text{Ce}_{3-x}\text{Mg}_x\text{Co}_9$ samples at 2 K parallel to c axis.
EDS inferred Mg concentrations $x = 0.01, 0.16, 0.24$ and $0.35$. In Figure 4, for the $\text{Ce}_{2.65}\text{Mg}_{0.35}\text{Co}_9$ sample, we can see an increasing low-field induced magnetisation upon cooling indicating that it may be getting close to a ferromagnetic transition. The lower right inset in Figure 4 shows ZFC and field cooled (FC) $M(T)$ data at 300 Oe applied field. This reversible nature of the $M(H)$ data argues against ferromagnetic transition for $T > 2.0$ K.

In order to study the $x = 0.35$, 0.43 and 0.50 samples in greater detail, $M(H)$ loops were performed as shown in Figures 4, 6, and 8 along with the determination of Curie temperature using the Arrott plot method as shown in Figures 5, 7 and 9. Within the framework of Arrott plot analysis,

![Figure 4](image1.png)

**Figure 4.** Field-dependent magnetisation of $\text{Ce}_{2.65}\text{Mg}_{0.35}\text{Co}_9$ at various temperatures to demonstrate only base temperature has some Brillouin-type saturation magnetisation. The lower inset shows the reversible nature of the ZFC and FC $M(T)$ data.

![Figure 5](image2.png)

**Figure 5.** The Arrott plot of $\text{Ce}_{2.65}\text{Mg}_{0.35}\text{Co}_9$ for $2 \leq T \leq 18$ K at a step of 4 K. The Curie temperature is suggested to be lower than 2 K. The inset shows the corresponding $M(H)$ data.
straight Arrott curves through the origin suggest a mean-field interaction in the magnetic system and identify the Curie temperature. The Arrott plot of \( x = 0.35 \) sample does not manifest straight lines that go through origin (as shown in Figure 5). This means that the Ce\(_{2.65}\)Mg\(_{0.35}\)Co\(_9\) is non-ferromagnetic down to 2 K despite the slight upturn in \( M(H) \) data. On the other hand, the Arrott plot data become straighter for Ce\(_{2.57}\)Mg\(_{0.43}\)Co\(_9\) (Figure 7 (b)) and almost an ideal mean-field-like for Ce\(_{2.50}\)Mg\(_{0.50}\)Co\(_9\) (Figure 9). From these analyses, we can infer \( T_C \approx 25 \) and 70 K for \( x = 0.43 \) and 0.50, respectively.

The 2 K \( M(H) \) data for \( x = 0.43 \) and 0.50 samples do not saturate up to 7 T applied field in these experiments, as shown in Figures 6 and 8. However, higher magnesium-containing samples, e.g. \( x = 1.34 \), were well saturated with 3 T applied field in our previous work [5]. This could be the evidence that the doping-induced magnetism is more itinerant for lower Mg content and becomes more local moment-like with a higher content of Mg. Though this question needs further investigation, our current speculation is following. Although Ce\(_{3-x}\)Mg\(_x\)Co\(_9\) has itinerant ferromagnetism, it does not show ideal Arrott plot as in ZrZn\(_2\), probably due to disorder effect created by Mg substitution. The counterintuitive observation is that the Arrott plot is being more and more ideal mean-field type as the concentration of Mg (disorder effect) becomes higher. This made us think that the ideal mean-field behaviour comes from the long-range local moment magnetism in Ce\(_{3-x}\)Mg\(_x\)Co\(_9\) with higher Mg.
Figures 10 and 11 present the $T_C - x$ and $M_S - x$ phase diagrams for the Ce$_{3-x}$Mg$_x$Co$_9$ system. Both figures identify $0.35 < x < 0.40$ as the critical concentration region for the quantum phase transition from a Pauli paramagnet to ferromagnetic state.

To further analyse the nature of the phase diagram and the quantum phase transition region, electrical transport properties of the samples around the critical composition and specific heat capacity of the ferromagnetic, $x = 0.50$ sample, were studied. Figure 12 shows the normalised resistance of Ce$_{3-x}$Mg$_x$Co$_9$ single crystalline samples for $x = 0.35$, 0.43 and 0.50. Figure 13 shows the temperature-dependent specific heat data for $x = 0.50$. Neither resistance nor specific heat data manifest clear signatures of ferromagnetic transitions. In the Stoner model, $\Delta C = M^2 / \chi_0 T_C$ would give a discontinuity around $2 \text{ J mol}^{-1} \text{ K}^{-1}$ at
For the resistance data, the anticipated loss of spin disorder features may be obscured by the clearly large and increasing disorder scattering. Additionally, doping disorder could have broadened the ferromagnetic transition so that transition feature was undetectable in resistance and specific heat measurements. The lack of a clear feature in specific heat for \( x = 0.50 \) suggests that there may be relatively little entropy loss associated with the

**Figure 8.** Field-dependent magnetisation of Ce\(_{2.50}\)Mg\(_{0.50}\)Co\(_9\) at various temperatures (Note: hysteresis at 2 K is larger than that shown for \( x = 0.43 \) as shown in Figure 6). The lower inset shows the \( M(T) \) along with the bifurcation of ZFC and FC \( M(T) \) data consistent with the observed low-temperature hysteresis loop.

**Figure 9.** The Arrott plot of Ce\(_{2.50}\)Mg\(_{0.50}\)Co\(_9\) for 50 K \( \leq T \leq 100 \) K at a step of 10 K. The Curie temperature is determined to be around 70 K. The inset shows the corresponding \( M(H) \) data. The demagnetisation factor \( N = 0.62 \) was used to get the internal field \( H_{\text{int}} = H - N \times M \).

For the resistance data, the anticipated loss of spin disorder features may be obscured by the clearly large and increasing disorder scattering. Additionally, doping disorder could have broadened the ferromagnetic transition so that transition feature was undetectable in resistance and specific heat measurements. The lack of a clear feature in specific heat for \( x = 0.50 \) suggests that there may be relatively little entropy loss associated with the

\( T_C \) for \( x = 0.5 \), but if spin fluctuation exists above \( T_C \) then discontinuity will be smaller [18].
transition. This is consistent with the small spontaneous moment (Figure 11) as well as with this system being a fragile, itinerant moment, ferromagnet.

4. Conclusions

The temperature-dependent magnetic, electrical transport properties and specific heat capacity of the low Mg content doped Ce$_{3-x}$Mg$_x$Co$_9$ samples
were studied using flux-grown single crystalline samples. From the $T_C$-$x$ phase diagram, the critical concentration for quantum transition between Pauli paramagnetic and ferromagnetic ground states is determined to be $0.35 \leq x \leq 0.40$.

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Disclosure statement

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