High-temperature ferromagnetism in the diluted magnetic semiconductor system lanthanum tantalum cobalt oxynitride

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Abstract

After two decades of research, we present the first semiconducting bulk high-temperature diluted ferromagnetic materials, based on the so far unknown perovskite-type oxynitrides LaTa$_{1-x}$Co$_x$(O,N)$_{3-d}$ ($x = 0.01, 0.03, 0.05$). The oxynitrides appear red with an optical bandgap of around 2 eV. An almost temperature-independent clear ferromagnetic saturative behaviour with coercive fields also present above room temperature was found by conventional and element specific magnetometry. The sample magnetisations were large enough to directly observe attracting forces by permanent magnets. Co clusters as a possible source for the observed high-temperature ferromagnetism can be excluded, since a variety of applied characterisation methods verify phase purity with a significant amount of anion vacancies. Therefore, we suggest these vacancies as an origin for a complex interaction between defect-like magnetism - as observed in many other oxides - and the introduced magnetic Co ions. The here reported results are highly relevant for semiconducting spintronics.

Main

In the year 2000 Dietl and co-workers predicted the possibility to obtain high-temperature ferromagnetism (HT-FM) above room temperature (RT) in a diluted magnetic semiconductor (DMS) via 3$d$ transition metal (TM) doping in semiconductors and insulators (ZnO or GaN)$^{1,2}$. They expected that $p$-type materials containing a critical concentration of holes and magnetic ions should exhibit an even higher Curie temperature ($T_c$) than (Ga,Mn)As or (Zn,Mn)Te:N$^1$. This prediction is very counter intuitive, since it is also well-known, that a strong prerequisite for RT-FM is a strong exchange interaction, which is not expected for large ionic distances$^3$. Nevertheless, this prospect$^1$ of a non-metallic or semiconducting ferromagnet, which could be used in new technologies, for example in spin-electronics$^4$, initiated a whole new field of magnetism research and was cited up to now about 7000 times. As charge-based electronics are nowadays dominated by the semiconducting electronics industries, a similar impact is expected for the field of spin-based electronics or spintronics$^5$. To tailor many of the magnetic properties (e.g. magnetisation, magnetocrystalline anisotropy etc.) the doping by ions or substitution of ions in a material should be a powerful tool. However, it was observed that the 3$d$ TM ions showed a paramagnetic behaviour, if they are homogeneously dissolved in the crystal matrix$^6,7$ or that simple TM clusters were responsible for parts of the ferromagnetic-like behaviour$^8$. In this context, new interesting magnetic phenomena such as the “$d^0$–magnetism” were found$^9-11$ where even undoped materials revealed ferromagnetic-like saturating magnetisation curves. As
examples we name TiO$_2^{12}$, pure ZnO in thin films$^{13}$ or pure pressed ZnO powders$^{14}$. This ferromagnetic-like behaviour was attributed to defect states, which are predominantly located at grain boundary sites$^{12,13,15}$. The real diluted ferromagnetic semiconductor behaviour for (Ga,Mn)As systems was only observed below 200 K$^{16}$. Therefore, no clear RT-ferromagnetism in true diluted bulk FM semiconductors was reported so far.

Perovskite-type oxynitrides $AB$(O,N)$_3$ are normally considered to be suitable for visible light-driven applications$^{17-22}$ or as cadmium-free inorganic pigments$^{23}$ because they exhibit an extraordinary flexibility in $A$- and $B$-site substitution with which the physical properties can be tuned$^{17,24-26}$. The previously reported LaTa(O,N)$_3$ system showed a clear non-magnetic semiconducting behaviour with very small effective magnetic moments and diamagnetism at RT$^{17}$. Therefore, it seems to be a promising matrix material for substitution with magnetic cations such as Co.

Since, actual diluted ferromagnetic semiconductors, such as (Ga,Mn)As systems, were only observed at lower temperatures, we present in this study evidence for a real bulk HT-FM DMS existing at temperatures far above RT. Our synthesised perovskite-type oxynitride LaTa$_{1-x}$Co$_x$(O,N)$_{3-\delta}$ ($x = 0.01, 0.03, 0.05$) reveals a clear and strong sample magnetisation even down to Co concentrations of only $x = 0.01$. The $x = 0.03$ and $x = 0.05$ samples can be even mechanically moved or attracted by permanent magnets. We also rule out the presence of spurious phases and FM metallic clusters as the origin of the observed HT-FM. LaTa$_{1-x}$Co$_x$(O,N)$_{3-\delta}$ is red and has an optical bandgap of around 2 eV and contains anionic vacancies. Hence, we report here the first real HT-ferromagnetic diluted semiconductor existing at temperatures above RT.
Results

Magnetism of the lanthanum tantalum cobalt oxynitrides

In the following, we present the first observation of bulk HT-FM in a DMS system as a function of Co substitution in the perovskite-type oxynitrides LaTa$_{1-x}$Co$_x$(O,N)$_{3-\delta}$ ($x = 0.01, 0.03, 0.05$). Figure 1a shows the mechanical movement of the $x = 0.05$ sample by permanent magnets (see also Supplemental Videos 1 and 2). Figures 1b-d show the by superconducting quantum interference device (SQUID) measured temperature-dependent magnetisation for different Co substitution levels of $x = 0.01, 0.03, 0.05$. The insets show the corresponding magnetisation reversal curves, with a focus in the flipping field range. Also, at room temperature a clear saturating behaviour is observed where 90 % of the saturation magnetisation ($M_s$) is already achieved at fields of about 3000 Oe.

Figure 1. Temperature-dependent magnetisation curves of LaTa$_{1-x}$Co$_x$(O,N)$_{3-\delta}$ ($x = 0.01, 0.03, 0.05$) and pictures showing the RT sample magnetism. a, Pictures and a scheme showing the mechanical movement of the HT-FM LaTa$_{0.95}$Co$_{0.05}$(O,N)$_{3-\delta}$ DMS by a permanent magnet which can be seen in the Supplemental Video 1 and 2. b-d, The magnetisation curves of LaTa$_{1-x}$Co$_x$(O,N)$_{3-\delta}$ ($x = 0.01, 0.03, 0.05$) show an almost temperature-independent ferromagnetic behaviour up to 350 K.
In addition, the insets also reveal a clear hysteretic behaviour, where the coercive fields are in the range of $137 \text{ Oe} \leq H_c \leq 192 \text{ Oe}$, which increase at low temperatures to $330 \text{ Oe} \leq H_c \leq 540 \text{ Oe}$ (Table 1). The RT saturation magnetisation $M_s$ increases with the amount of Co from 0.088 emu·g$^{-1}$ to 1.23 emu·g$^{-1}$ (Table 1).

**Table 1. Extracted magnetic parameters.** The extracted magnetic parameters are the coercive fields $H_c$, saturation magnetisation $M_s$, and effective magnetic moment $m_{Co}$ per Co ion for each Co concentration.

| $x_{Co}$ | $H_c$ (Oe) | $M_s$ (emu·g$^{-1}$) | $m_{Co}$ ($\mu_B$) |
|----------|------------|----------------------|-------------------|
| 0.01     | 540 (1.8 K) 137 (RT) | 0.088 | 0.60 |
| 0.03     | 260 (10 K) 192 (RT) | 0.543 | 1.29 |
| 0.05     | 320 (10 K) 160 (RT) | 1.23 | 1.55 |

It is also observable that all presented LaTa$_{1-x}$Co$_x$(O,N)$_{3-\delta}$ samples reveal an increase of paramagnetic-like behaviour with similar absolute value at low temperatures, but larger relative contribution for low Co concentrations (Fig. 1 and Supplementary Note 1 and 2). For example, LaTa$_{0.99}$Co$_{0.01}$(O,N)$_{3-\delta}$ has a Curie-like relative increase with respect to the FM-like behaviour of about $60 \%$. In comparison, for LaTa$_{0.95}$Co$_{0.05}$(O,N)$_{3-\delta}$ it is only of about $4 \%$. Therefore, we attribute the paramagnetism to defect-like states, which are similar in strength for all three samples. In addition, a clear increase in the magnetic moment per Co ion is observed. If we attribute the whole sample magnetisation to the given amount of Co ions, we can calculate an effective magnetic moment per Co ion, increasing from $0.6 \mu_B$/Co to $1.55 \mu_B$/Co (Table 1). At this point it is to emphasize that in case of the attracting permanent magnet always the whole amount of sample powder was attracted.

In order to identify possible different contributions to the sample magnetisation, X-ray absorption spectroscopy (XAS) / X-ray magnetic circular dichroism (XMCD) at the Co-$L_{2,3}$ edge were performed (Figure 2). In Figure 2a, the surface-sensitive total electron yield (TEY) non-magnetic XAS spectra for all three Co concentrations reveal a clear multiplet-like peak structure, very similar to Co$^{2+}$ 27-29. The corresponding XMCD signal is shown for LaTa$_{0.95}$Co$_{0.05}$(O,N)$_{3-\delta}$. Considering the given noise limit no clear XMCD signal could be observed.
Figure 2. XAS/XMCD edge normalised at the Co-\(L_{2,3}\) edges. 

**a**, TEY spectra for all three Co concentrations of LaTa\(_{1-x}\)Co\(_x\)(O,N)\(_{3-\delta}\) (vertically shifted for better visibility). 

**b**, Corresponding TFY mode XAS/XMCD for LaTa\(_{0.95}\)Co\(_{0.05}\)(O,N)\(_{3-\delta}\).

Figure 2b shows the corresponding more bulk-sensitive total fluorescence yield (TFY) spectrum of LaTa\(_{0.95}\)Co\(_{0.05}\)(O,N)\(_{3-\delta}\). This TFY spectrum is a superposition of 48 single measurements to provide a reasonable signal to noise ratio. A clear XMCD signal can be observed which has a relative intensity with respect to the Co white line of about 14%. Compared to the surface-sensitive TEY signal, the peak shape is quite different and - from the first view - closer to typical Co metal-like spectra (no peak splitting and asymmetric shape). However, other perovskite-type Co-containing oxides with Co\(^{3+}\) in octahedral coordination (e.g. LaCoO\(_3\)) reveal also Co-\(L_{2,3}\) edge spectra with similar spectral shape. On the one hand, it is well known, that the shape and white line intensity are significantly modified in TFY spectra due to self-absorption phenomena. On the other hand, the white line intensity or the \(L_3\) edge damping is true for strong resonances, but not for diluted atoms. In the case of LaTa\(_{0.95}\)Co\(_{0.05}\)(O,N)\(_{3-\delta}\) one Co ion is present for 99 La, Ta, O, and N atoms, meaning just 1 at% Co in the whole sample. This reduces self-absorption phenomena significantly, which encourages us to apply sum rules to quantify the TFY-XMCD. Because, the Co valence state in the sample is unknown we can just assume the number of 3\(d\) holes as for metallic Co for the sum rule application. Therefore, we estimate a spin moment of only 0.9 \(\mu_B/\text{Co}\) and an almost vanishing orbital moment of 0.01 \(\mu_B/\text{Co}\) by using the pure Co metal number of holes \(n_H = 2.49\). As discussed above, the TFY spectral shape indicates at least the partial presence of Co\(^{3+}\). In the case, if only Co\(^{3+}\) in the bulk is present, we would have a 3\(d^0\) configuration with \(n_H = 4\) and it would lead to a spin moment of up to 1.44 \(\mu_B/\text{Co}\) and an orbital moment of 0.02 \(\mu_B/\text{Co}\). According to the TEY/TFY spectra a Co oxidation state variety
between 2+ (surface) and 3+ (bulk) in our samples can be assumed. This comes from the fact, that the used synthesis method of ammonolysis (see section ”Formation and characterisation of the HT-ferromagnetic oxynitride”) is including a solid-gas-interface reaction where the reducing species react first with the samples’ surface and lead to an enhanced reduction of the B-site cations which are located close to the surface\textsuperscript{17}. Therefore, an oxidation state gradient from the surface (Co\textsuperscript{2+} according to TEY) to the bulk (partial Co\textsuperscript{3+} according to TFY) can be assumed and a mixture of different Co oxidation states in the bulk cannot be excluded. This would result in different spin and orbital moments as observed for pure Co\textsuperscript{3+}. By comparing the determined effective magnetic moments of the LaTa\textsubscript{0.95}Co\textsubscript{0.05}(O,N)\textsubscript{3–δ} sample for pure Co\textsuperscript{3+} by TFY-XMCD (1.44 \(\mu_B\)/Co, see above) and that of SQUID (1.55 \(\mu_B\)/Co) a smaller difference in the determined magnetic moments between both methods is observed.

As we will discuss later in the section “Proof of HT-ferromagnetism in the perovskite-type oxynitride“, we have a significant amount of anion vacancies present in our system which can also contribute to the magnetism. For the moment, it is not clear, how and if these vacancies are correlated to the Co ions. Additionally, it also cannot be answered now, if charge transfer phenomena between Co and the neighbouring Ta ions are present, because several valence variations for both cations are possible. Despite the fact, that we can clearly verify Co-based magnetism here, the Co effective magnetic moments on the basis of XMCD remain as an open question so far. Furthermore, we would like to mention that the determined saturation magnetisations and effective magnetic moments for all synthesised samples were highly reproducible by measuring different batches.

**Formation and characterisation of the HT-ferromagnetic oxynitride**

The \textit{ex situ}\textsuperscript{17} ammonolysis of nanoparticulate and nanocrystalline n-LaTa\textsubscript{1–x}Co\textsubscript{x}O\textsubscript{4–δ} (x = 0.01, 0.03, 0.05) precursors in a conventional thermal gas flow ammonolysis setup leads to the before unknown perovskite-type oxynitrides LaTa\textsubscript{1–x}Co\textsubscript{x}(O,N)\textsubscript{3–δ} (x = 0.01, 0.03, 0.05) containing particles in the nm-range (Fig. 3a-f).
Figure 3. In situ ammonolysis of $n$-LaTa$_{1-x}$Co$_x$O$_{4-\delta}$ ($x = 0.01, 0.03, 0.05$), the respective scanning electron microscopy (SEM) images, and sample photos. a-f, Respective SEM images of $n$-LaTa$_{1-x}$Co$_x$O$_{4-\delta}$ ($x = 0.01, 0.03, 0.05$) showing primary particles in the nm-range and of LaTa$_{1-x}$Co$_x$(O,N)$_{3-\delta}$ showing nanoparticles with the respective sample photos. Scalebar of the SEM images: 1 µm. g, In situ ammonolysis (10 vol% Ar in NH$_3$) of LaTa$_{1-x}$Co$_x$O$_{4-\delta}$ ($x = 0.01, 0.03, 0.05$). The reaction steps are similar to those of LaTa$_{IV}$O$_2$N$_{17}$ on the first view. However, some differences are observed by the use of $n$-LaTa$_{1-x}$Co$_x$O$_{4-\delta}$ ($n$-LaTa$_{1-x}$Co$_x$O$_y$$\square_z$): The present oxygen vacancies lead to a continuous flattening of the local maximum between 1050 K and 1223 K (inset, Fig. 3g) and to an anionic ratio of nearly O:N = 1:2 in LaTa$_{1-x}$Co$_x$(O,N)$_{3-\delta}$. The compositions are explicitly given in order to show the vacancy concentration. The obtained curve progressions (black, red, and blue) lay in between the curve progressions of the unsubstituted nanocrystalline lanthanum tantalum oxide $n$-LTO (green) and microcrystalline m-LaTaO$_4$ (orange). The shown reference samples $n$-LTO and m-LaTaO$_4$ are synthesised according to ref. 17. The dashed line represents the temperature.

The compositions and phase purities of the oxides and the compositions of the oxynitrides are treated in detail in the Supplementary Notes 3-5, Supplementary Figures 3-5, and Supplementary Tables 1-3. Powder X-ray diffraction (PXRD) and neutron diffraction (ND) give no hint of a secondary phase for all three Co concentrations.
Therefore, we assume for all LaTa$_{1-x}$Co$_x$(O,N)$_{3-\delta}$ ($x = 0.01, 0.03, 0.05$) samples phase purity (Supplementary Note 6, Supplementary Fig. 6-9, and Supplementary Tables 4-7). Rietveld refinements of the diffraction patterns reveal $Imma$ as space group type pointing to a perovskite-type phase. The same space group type was already reported for the perovskite-type oxynitrides LaTaO$_2$N and LaTaON$_2$ and seems plausible, since, we used very small amounts of Co for $B$-site substitution in the system LaTa(O,N)$_3$. By having a closer look at the unit cell parameters and unit cell volumes, no clear trend is observed (e.g. Supplementary Table 4a). As mentioned before that Co$^{2+}$ on the surface and Co$^{3+}$ in the bulk for the LaTa$_{0.95}$Co$_{0.05}$(O,N)$_{3-\delta}$ sample could be determined by XAS. However, for X-ray photoelectron spectroscopy (XPS) investigations in order to determine the Ta and Co oxidation states the amount of Co ($\leq 1$ at%) was too low to determine its’ oxidation state for all Co concentrations (Supplementary Note 7 and Supplementary Fig. 10). Therefore, additional information of the Co oxidation state and therewith the effective ionic radii of the $B$-site cations for all samples is missing and we cannot use them to explain the changes in unit cell volumes and unit cell parameters as already done for LaTaO$_2$N.

The colours of the LaTa$_{1-x}$Co$_x$(O,N)$_{3-\delta}$ ($x = 0.01, 0.03, 0.05$) powders are ranging from red ($x = 0.01$) via dark red ($x = 0.03$) to a very dark red ($x = 0.05$) (Fig. 3 d-f), which represents the spectroscopically observed enhanced diffuse reflectance below the bandgap energy of about 2 eV at increasing Co concentrations (Supplementary Note 8 and Supplementary Fig. 11). The red colour hints to a semiconducting material. Supporting this, metallic nanopowders are typically black in colour. In addition, the edge like almost flat shape at larger wavelengths of the diffuse reflectance spectra (DRS) suggest a semiconductor without the presence of metallic clusters (Supplementary Note 8).

By comparing the formation of LaTa$_{1-x}$Co$_x$(O,N)$_{3-\delta}$ from n-LaTa$_{1-x}$Co$_x$O$_{4-\delta}$ with the in literature reported LaTaO$_2$N formation from nanocrystalline lanthanum tantalum oxide (n-LTO) several differences are observed. Normally, the oxynitride formation from n-LTO can be described by three simultaneous processes which occur during the ammonolysis: oxygen vacancy formation, nitrogen incorporation, and $B$-site cation reduction ($Ta^{5+}$ to $Ta^{4+}$) leading to an oxynitride with an anionic ratio of O:N = 2:1 and product particles in the nm-range. In our case we obtain a product in-between, namely LaTa$_{1-x}$Co$_x$(O,N)$_{3-\delta}$, with an anionic ratio of nearly O:N = 1:2 (Supplementary Table 2), anionic vacancies, no Ta$^{4+}$, and particles in the nm-range (Supplementary Note 7 and 9 and Supplementary Fig. 10, 12, and 13). Since, the oxidation states of Co in the oxide cannot be clarified because of the detection limits of X-ray photoelectron spectroscopy (XPS) and XAS, we assume that the present oxygen vacancies in n-LaTa$_{1-x}$Co$_x$O$_{4-\delta}$ are the driving force leading to a reaction progression intermediate to microcrystalline LaTaO$_4$ (m-
LaTaO₄) and n-LTO (Fig. 3g). Additionally, we suggest that these vacancies hamper the reduction from Ta⁵⁺ to Ta⁴⁺, since, no Ta⁴⁺ was found in the obtained oxynitride products by XPS (Supplementary Fig. 10). Therefore, we can add besides the recent reported microstructure of the oxide precursor¹⁷ the presence of oxygen vacancies in the oxide precursor as parameter to tailor the oxidation state of B-site cations in oxynitride phases. To conclude this section, we synthesised a red semiconducting perovskite-type oxynitride, which is according to crystal structure and chemical analysis phase pure.

**Proof of HT-ferromagnetism in the perovskite-type oxynitride**

The main remaining task now, is to exclude as far as possible other extrinsic magnetic phenomena as a possible source for the observed HT-FM. In former reports undesired TM clusters were responsible at least for some parts of the measured magnetisation curves⁸,³⁹,⁴⁰. In our case, we can exclude the presence of TM clusters as a possible source for HT-FM, as we discuss in the following:

Transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDX) analysis showed no hints of Co metal-like clusters larger than 4 nm (Fig. 4). The recorded EDX maps show clearly a very homogeneous distribution (2 nm per pixel) of the B-site cations Co and Ta excluding, both, Co metal-like clusters and secondary Co-rich phases (Fig. 4d-f). Every yellow, single pixel is related to Co EDX single photon count, which is consistent to perfectly diluted Co ions. If Co would be segregated to very small Co clusters, a strong signal increase above the average counting rate of Ta would be expected, which is not the case. The materials contrast of the particles in Fig. 4a-c can be attributed to different crystal orientations (Fig. 4g-i) proven by a recorded selective area diffraction pattern (Supplementary Fig. 14). All powders are polycrystalline and all rings can be completely indexed by *Imma* without leaving additional rings for secondary phases (Supplementary Fig. 14). Despite, the statistical character of the Co EDX results, the estimated Co amount is consistent to the total amount of Co in our samples, showing that the Co XMCD signal is indeed related to Co solved in the LaTa(O,N)₃ matrix. Nevertheless, since TEM is always representing a selected number of arbitrarily sample cutouts, we cannot perfectly exclude a very small amount of Co rich phases just from TEM investigations.
Figure 4. Transmission electron microscopy (TEM) of LaTa$_{1-x}$Co$_x$(O,N)$_{3-\delta}$ ($x = 0.01, 0.03, 0.05$). a-c, TEM images of particles of LaTa$_{1-x}$Co$_x$(O,N)$_{3-\delta}$ ($x = 0.01, 0.03, 0.05$) and d-f, EDX maps of of LaTa$_{1-x}$Co$_x$(O,N)$_{3-\delta}$ ($x = 0.01, 0.03, 0.05$) showing the homogeneous distribution of Co (yellow) and Ta (pink) in the particles. Co clusters or Co-rich secondary particles with a size larger than 4 nm can be excluded. g-i, The dark field TEM images show in different colours the different crystal orientations of the particles. Scalebar of all images: 100 nm.

Because, small Co clusters shall reveal superparamagnetic behaviour, we compared the Langevin function-like $M(H)$ curves for different temperatures with the measured ones (Supplementary Note 1). The calculated superparamagnetic curves for Co clusters reveal a very strong temperature dependency, which is not observed for our samples, providing a second proof for the absence of Co clusters. In order to identify a clear volume magnetic effect, we performed anisotropic $M(H)$ curves for in- and out-of-plane directions of a flat pressed pellet sample (Supplementary Note 2). If the observed HT-FM is really a volume effect, a clear demagnetising field related anisotropic difference should be present scaling with the achieved sample magnetisation. As shown in
Supplementary Note 2, this was observed indeed, and the difference between in- and out-of-plane curves can be perfectly modelled using the sample volume magnetisation, shape, and related demagnetisation factors. On the other hand, even larger Co clusters\textsuperscript{41} and Co particles (own reference data, not shown), respectively, reveal direct observable and strong temperature dependencies in saturation magnetisation, shape and coercive fields between 10 K and RT. These magnetic features are not observed for LaTa\textsubscript{1-x}Co\textsubscript{x}(O,N)\textsubscript{3-δ} (x = 0.01, 0.03, 0.05). The chemical reaction conditions (ammonolysis of an oxide) used to synthesise LaTa\textsubscript{1-x}Co\textsubscript{x}(O,N)\textsubscript{3-δ} (x = 0.01, 0.03, 0.05) are unlikely to form pure metallic Co.

Our preliminary explanation in the section “Magnetism of the lanthanum tantalum cobalt oxynitride” for the observed DMS HT-FM is somewhat similar to previous explanations for pure ZnO RT-FM. In this compound surface related vacancies were identified to explain ferromagnetic coupling, where off-stoichiometric grain boundaries made a FM foam like structure\textsuperscript{13–15}. This is also consistent to recent studies on highly defective 2D ZnO nanosheets\textsuperscript{42}. Since, our LaTa\textsubscript{1-x}Co\textsubscript{x}(O,N)\textsubscript{3-δ} contains a significant amount of anion vacancies (Supplementary Note 5), we conclude that even the volume effect could be similar to the vacancy dominated FM foam as discussed in other d\textsuperscript{9} FM materials\textsuperscript{13–15}. Hence, the matrix is highly polarisable but not ferromagnetic by itself and the interplay with the Co could provide the necessary ferromagnetic order. This is supported by the Co XMCD sum rule results, which seem to provide a smaller Co magnetisation compared to the SQUID based values. The obtained possible difference between both methods could be easily explained, if about one third of the total magnetisation is related to the magnetically polarised volume, also providing the necessary long-range exchange coupling strength between the far distant Co ions.

**Summary**

In this study we present an almost temperature-independent FM behaviour in a DMS LaTa\textsubscript{1-x}Co\textsubscript{x}(O,N)\textsubscript{3-δ} system, with a Curie temperature \( T_c \) exceeding 350 K. The observed saturation magnetisation increases with the amount of Co and is large enough to allow mechanical movement of the powder by external magnetic forces, generated from commercially available permanent magnets (Supplementary Video 1 and 2). All three synthesised perovskite-type oxynitrides LaTa\textsubscript{1-x}Co\textsubscript{x}(O,N)\textsubscript{3-δ} (x = 0.01, 0.03, 0.05) are single phase according to crystal structure and chemical analysis compositions and the formation could be clarified. To conclude, after two decades of intensive research in the magnetism community, we report the first observation of clear and relatively strong bulk HT-FM in a diluted semiconducting material.
Methods

Synthesis of \( \text{n-LaTa}_{1-x}\text{Co}_x\text{O}_{4-\delta} \) \( (x = 0.01, 0.03, 0.05) \). The oxides were prepared \textit{via} a Pechini method which is based on the already reported one for \( \text{n-LTO}^{17} \). First, \( \text{TaCl}_5 \) (Alfa Aesar, 99.99 %) and \( \text{Co(NO}_3\text{)}_2\cdot6\text{H}_2\text{O} \) (Merck, EMSURE®) were loaded in a stoichiometric amount into a Schlenk flask under argon and 50 mL of dried methanol was added. The molar mass of the \( B \)-site cations Ta and Co was calculated to be 0.01 mol in total. Afterwards, 0.03 mol water-free citric acid (Sigma Aldrich, ≥ 99.0 %) was added. 0.01 mol \( \text{La(NO}_3\text{)}_3\cdot6\text{H}_2\text{O} \) (Sigma Aldrich, 99.99 %) was weighed into a second Schlenk flask and citric acid was added in the same molar ratio as for the \( B \)-site cations. The mixture was dissolved in 10 mL of dried methanol and the solutions of both Schlenk flasks were combined in one Schlenk flask and stirred under reflux for 2 h at 353 K with addition of a 15-fold molar excess of ethylene glycol (Merck, EMPLURA®). The dispersion was transferred to a crystallising dish and heated for 10 h at 393 K followed by a thermal treatment at 573 K for 5 h as reported before\(^17\). The resulting black xerogel was calcined in an alumina crucible for 16 h at 923 K to obtain the nanocrystalline \( \text{n-LaTa}_{1-x}\text{Co}_x\text{O}_{4-\delta} \) \( (x = 0.01, 0.03, 0.05) \).

Synthesis of \( \text{LaTa}_{1-x}\text{Co}_x(\text{O,N})_{3-\delta} \) \( (x = 0.01, 0.03, 0.05) \). 350 mg of \( \text{n-LaTa}_{1-x}\text{Co}_x\text{O}_{4-\delta} \) \( (x = 0.01, 0.03, 0.05) \) was loaded into an alumina boat and placed into a conventional thermal gas flow ammonolysis setup. Ammonolysis was carried out for 10 h at 1223 K with two subsequent ammonolysis cycles for 14 h at 1273 K and KCl flux addition (1:1 weight ratio). The applied ammonia flow for all cycles was 300 mL·min\(^{-1}\) \( \text{NH}_3 \) (Westfalen AG, > 99.98 %).

Sample Characterisation. Powder X-ray diffraction (PXRD) measurements at RT were carried out on a Bruker D8-Advance powder X-ray diffractometer using Cu-\( \text{K}_\alpha_1 \) radiation (Ge(111) monochromator), Bragg Brentano geometry, and a Lynx-Eye detector and on a Rigaku Smartlab powder X-ray diffractometer (Cu-\( \text{K}_\alpha_1,2 \)). The continuous scans covered an angular range of \( 5^\circ \leq 2\theta \leq 90^\circ \) with an angular step interval of 0.007°. The collected diffraction data were evaluated \textit{via} Rietveld refinements\(^{43,44}\) using \textit{FullProf}. 2k\(^45\). Pseudo-Voigt functions were selected to describe the reflection profile and the background was linearly interpolated between a set of background points with refinable heights.
The chemical composition of the produced samples was investigated via inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Spectro Ciros CCD ICP-OES instrument for cations and hot gas extraction technique (HGE) using an Eltra ONH-2000 analyser for the anions.

*In situ* ammonolysis\(^\text{17}\) was performed by thermogravimetric analysis (TGA) by using a Netzsch STA 449 F3 Jupiter and were carried out under flowing NH\(_3\) (80 mL·min\(^{-1}\) NH\(_3\) + 8 mL·min\(^{-1}\) Ar) with a heating rate of 10 K·min\(^{-1}\) up to 1273 K.

X-ray photoelectron spectroscopy (XPS) was carried out using a Kratos Axis Ultra system with a monochromatised Al-\(K_a\) source (1486.6 eV) holding a base pressure in the lower 10\(^{-10}\) mbar range. The powders were fixed on an indium foil and a flood gun was used in order to avoid charging effects. The binding energy was calibrated by setting the C 1\(s\) of adventitious carbon to 284.5 eV with respect to the Fermi level. Analysis of the XPS data was performed with Casa XPS software. The energy separation and peak area of the Ta 4\(f_{7/2}\) and Ta 4\(f_{5/2}\) were constrained according to literature\(^\text{46}\). The low signal to noise ratio together with a non-flat background did not allow for any reasonable fitting of the Co 2\(p\) region.

The particle morphology of the produced LaTa\(_{1-x}\)Co\(_x\)(O,N)\(_{3-\delta}\) and n-LaTa\(_{1-x}\)Co\(_x\)O\(_{4-\delta}\) was analysed via scanning electron microscopy (SEM) (ZEISS GeminiSEM 500, 2 kV) and the in-lens detector was used for imaging.

UV-visible diffuse reflectance spectra (DRS) were recorded by using a Carry 5000 UV–VIS NIR spectrophotometer. The spectra were measured in the range of 200 nm to 800 nm and the Kubelka-Munk\(^\text{47}\) conversion was applied to the recorded reflectance spectra. The optical bandgaps were estimated by extrapolating the onset of absorption to the abscissa.

Magnetometer surveys were carried out with a commercial VSM MPMS3 Superconducting Quantum Interference Device (SQUID) from Quantum Design. This system allows both conventional DC and VSM-type measurements. The temperature ranged from 1.8 K up to 350 K, while the field was switched up to 7 T. For zero field cooling purposes the magnet was quenched to minimize the residual magnetic field. Depending on the sample and the measurement type the effective sensitivity was in the range of 10\(^{-8}\)-10\(^{-9}\) emu. The pressed powder anisotropy measurements in Supplementary Note 2 were performed with a Quantum Design MPMS 7 system, because the detection system is less sensitive for variations in the filling factor, providing better precision and comparability for anisotropic sample geometries.

The particles of LaTa\(_{1-x}\)Co\(_x\)(O,N)\(_{3-\delta}\) (\(x = 0.01, 0.03, 0.05\)) were dispersed in ethanol and drop casted on a Cu grid covered with an amorphous carbon foil and with a mesh size of 200 μm provided by Plano. Small accumulations of oxynitride and oxide particles, respectively, were investigated on a Philips CM-200 FEG TEM operated at 200 kV.
applying bright- and dark-field imaging. In order to verify the space group determined by Rietveld refinements of the PXRD and ND data, selected area diffraction patterns were recorded. The recorded polycrystalline diffraction patterns were analysed by using the JEMS software package. Colour grain orientation maps were constructed by the overlay of five dark-field images recorded with varying beam tilt. The composition and homogeneity of selected particles was analysed with an energy dispersive X-ray (EDX) spectroscopy system from EDAX. Elemental mappings were collected with a probe size of 3 nm, a step size of ~2 nm and a dwell time of 15 ms per pixel.

X-ray magnetic circular dichroism (XMCD) and X-ray absorption spectroscopy (XAS) experiments were performed at the synchrotron ANKA/KARA at KIT, Karlsruhe, in order to measure local atomic magnetic moments. All XMCD and XAS spectra were recorded at the WERA beamline with an energy resolution of about \( \Delta E/E = 2 \cdot 10^{-4} \). We used our own superconducting magnet end station providing ultra-fast field switching with ramping rates up to 1.5 T/s. All spectra were measured in an applied magnetic field up to 6.5 T. Each XMCD spectrum was measured as a function of energy with fixed light helicity and field. The energy was swiped uniformly with a rate (monochromator speed) of 0.2 eV/s measured for each spectrum while simultaneously reading out the total electron yield (TEY), total fluorescence yield (TFY), and incident X-ray (Au grid for \( I_0 \)) current with about one data point every 0.03 eV. The photocurrent from up to 4 Hamamatsu GaAsP photodiodes (G 1740 type) with an active area of 5.6×5.6 mm\(^2\) was measured to provide the TFY signal. In order to get the XMCD data the circular light helicity was chosen (R = right, L = left), then two measurements were performed with reversed magnetic field (N = north; S = south). The sequence for a single full step run was 

\[
\text{RN} \rightarrow \text{RS} \rightarrow \text{LN} \rightarrow \text{LS} \rightarrow \text{LN} \rightarrow \text{LS} \rightarrow \text{RN} \rightarrow \text{RS}.
\]

This sequence minimized the effects of drift and further possible systematic errors. For better statistics, final spectra were averaged over many consecutive spectra (in both helicities). This kind of measurement series were repeated until the desired signal to noise ratio was achieved. TEY, TFY, and \( I_0 \) were measured using Keithley 6517A electrometers. The ramping rate (0.2 eV·s\(^{-1}\)) was carefully chosen that no observable energy broadening could be detected. Each single XAS spectrum took about 3-5 minutes. No noticeable energy drift was observed between consecutive single spectra. Nonmagnetic XAS spectra were obtained by averaging the magnetic XAS spectra for parallel and antiparallel aligned light helicity vs. magnetisation direction.

Neutron diffraction (ND) was carried out on the high-resolution D2B diffractometer (\( \lambda = 1.59417(2) \) Å) of the Institut Laue Langevin (ILL). The diffractograms of LaTa\(_{1-x}\)Co\(_x\)(O,N)\(_{3-\delta}\) (\( x = 0.01, 0.03, 0.05 \)) were recorded at 10 K and 300 K. The ND data (DOI: 10.5291/ILL-DATA.EASY-471, 10.5291/ILL-DATA.EASY-472,
10.5291/ILL-DATA.6-06-482) was refined using the *FullProf* 2k and a pseudo-Voigt function was chosen to generate the line shape of the reflections. No magnetic refinement of the data was possible as due to the low amount of Co present in the samples (Ta is assumed to be non-magnetic) any magnetic contribution to the scattering falls short of the detection limit of neutrons.

In order to investigate the specific surface area of the oxide precursors nitrogen sorption was carried out using an Autosorb-1-MP (Detection limit: $S_{BET} > 1 \text{ m}^2/\text{g}$) from Quantachrome Instruments. First, the samples were annealed at 393 K in order to remove adsorbed water. Adsorption and desorption isotherms were collected at 77 K. To determine the specific surface area the Brunauer-Emmett-Teller ($^4$BET) method was used.

To determine possible adsorbed water and organic residues on the oxide precursors’ surface TGA-MS was carried out on a Netzsch STA 449 C Jupiter coupled with a QMS 403C Aeolos® mass spectrometer. The oxide was heated to 1473 K at a rate of 5 K·min$^{-1}$ under synthetic air and then cooled to room temperature.

**Data Availability**

Supplementary information is available in the online version of the paper and supplementary digital data such as supplementary videos is added to the online version. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence should be addressed to E.G. and A.W.

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**Author Contributions**

C.B. developed and synthesised the oxide precursors and the perovskite-type oxynitrides, performed and analysed SEM, DRS, TGA, and *in situ* ammonolysis. C.B. refined and analysed the PXRD data. C.B found the magnetism in the perovskite-type oxynitrides, whereas E.G. provided the original interpretation of the HT-ferromagnetism of the compounds. E.G. performed and analysed the magnetic measurements with data contribution from C.B. The XMCD/XAS measurements were carried out by E.G., C.B., P.N. and S.S. and the respective data was analysed by E.G. E.G. and C.B. analysed together the XAS data. G.S., P.N., M.M. and S.S. contributed to the discussion of the XMCD and XAS data. R.L. and C.B. measured and analysed together TEM/EDX. K.K. performed the XPS measurements and analysed the data together with C.B. U.S. provided discussion to the XPS part. M.W. and A.W. contributed to the discussion of the *in situ* ammonolysis. C.B., G.J.C. and M.W. measured together neutron diffraction. The ND data was refined and analysed by C.B., whereas C.R., G.J.C. and M.W. contributed to the discussion of the ND data. C.B. and E.G. wrote together the paper and A.W. provided final contributions to the conclusions.

**Competing Interests**

The authors declare no competing interests. All authors approved the submission of the manuscript.