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Tunability of the spin reorientation transitions with pressure in NdCo$_5$ 

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We present pressure-dependent magnetization measurements carried out in the domain of the spin reorientation transitions (SRTs) of a NdCo$_5$ single crystal. The application of a hydrostatic pressure leads to a shift in the SRTs to higher temperatures. This shift is found to be very sensitive to pressure, with the SRT temperatures increasing at a rate of $\approx 17$ K/GPa. To explain the experimental results, we have also performed first-principles calculations of the SRT temperatures for different applied strains which corroborate the experimental findings. The calculations attribute the pressure dependence of the SRTs to a faster weakening of the Co contribution to the magnetocrystalline anisotropy with pressure compared to the Nd contribution.

The class of intermetallic compounds with the formula RCo$_5$ (R = rare earth) are archetypal rare-earth transition-metal permanent magnets, displaying high Curie temperatures, large saturation magnetizations and strong magnetic anisotropy, and have been the subject of intensive investigations both experimentally and theoretically for several decades. RCo$_5$ crystallizes in the hexagonal P6/mmm structure with RCo$_2$ planes interspersed with Co planes. Magnetically, RCo$_5$ is a ferrimagnet whose properties derive from two magnetic sublattices associated with the rare earth and the cobalt atoms. Competition between these sublattices can lead to unusual magnetic behavior, especially as a function of temperature. For example, in GdCo$_5$ the Gd sublattice, whose moments are aligned antiparallel to the Co moments through an antiferromagnetic exchange interaction, disorders more quickly with temperature than the Co sublattice and so the magnetization increases with temperature, reaching a peak around 800 K. This faster disordering of the R sublattice is observed across the RCo$_5$ series because of the weaker exchange interactions for R-Co than Co-Co. The antiferromagnetic exchange originates from a strong hybridization of the minority Co-3d and the R-5d bands. The majority Co-3d band, with lower energy, is unable to undergo this hybridization.

The competition between the R and Co sublattices also causes the magnetocrystalline anisotropy (MCA) to behave unusually. The MCA associated with the itinerant electrons forming the Co sublattice favors magnetization parallel to the crystallographic c-axis for all members of the RCo$_5$ family. However, the MCA of the R moments originates from the R-4f electrons interacting with the crystal field, and whether this interaction favors c-axis or ab-plane magnetization depends on R. Among the lighter rare earths, R does not contribute to the MCA for Y and La, and reinforces the c-axis anisotropy for Ce and Sm. Only in PrCo$_5$ and NdCo$_5$ does the R contribution to the MCA favor ab plane magnetization, competing with the uniaxial anisotropy of the Co moments. For PrCo$_5$ the Pr contribution to the MCA is relatively weak, so at cryogenic temperatures the magnetization points $23^\circ$ from the c-axis, and aligns along c at temperatures above 105 K. However, in NdCo$_5$ the MCA associated with Nd is strong enough to overcome the Co anisotropy, so the resultant magnetization lies in the ab plane at low temperature.

As the temperature of NdCo$_5$ is raised, a faster disordering of the R sublattice weakens the Nd planar MCA compared to the uniaxial Co contribution. At a critical temperature $T_{SR1}$, the magnetization starts to rotate towards the c-axis (cone anisotropy). This rotation completes at $T_{SR2}$, when the magnetization points along the c-axis. The transitions from planar cone and cone c-axis alignment are referred to as spin reorientation transitions (SRTs). The SRTs of NdCo$_5$ have been the subject of a number of studies, and are considered particularly interesting because $T_{SR1}$ and $T_{SR2}$ are not far from room temperature, at approximately 240 and 290 K, respectively. This work includes our study of NdCo$_5$ using torque magnetometry, investigating the underlying physics and location of the SRTs. Interest in NdCo$_5$ was increased further by the discovery of a giant rotating magnetocaloric effect in NdCo$_5$ with a maximum adiabatic temperature change observed at 280 K, close to $T_{SR2}$, suggesting this material could be used in magnetic refrigeration. This observation inspired attempts to bring the operating temperature of the magnetocaloric cycle closer to room temperature, by manipulating $T_{SR2}$.

Any changes in the R or Co MCA will affect the SRT temperatures. Crucially, however, since the SRT temperatures are determined by the balance between sublattices, it is the relative MCA enhancement which determines how the SRT temperatures change. Strengthening the R contribution relative to Co will favor planar alignment over a wider temperature range increasing $T_{SR1}$ and $T_{SR2}$. Conversely, strengthening the Co uniaxial anisotropy relative to R will decrease $T_{SR1}$ and $T_{SR2}$.

To date, attempts to change $T_{SR2}$ of NdCo$_5$ have focused on introducing dopant atoms. For instance, substituting Co with B to form NdCo$_5$B increases the relative strength of the planar contribution to the extent that planar anisotropy dominates all the way to the Curie temperature, so that no SRT is observed. Substitution with Al or Si to form NdCo$_5$Al or NdCo$_5$Si also shifts the balance in favor of planar anisotropy, but by a lesser extent than in NdCo$_5$B. Accordingly, these compounds still exhibit SRTs, and at elevated temperatures compared to NdCo$_5$. However, the precise mechanism by which dopant atoms affect the SRTs is not easy to identify. Apart from modifying the electronic band structure, which will alter the Co anisotropy, the introduction of dopants will possibly change the crystal field at the R site.

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both through local interactions and also a global modification of the lattice parameters.

In this Letter, we demonstrate an alternative method to manipulate the SRTs by placing NdCo$_5$ under hydrostatic pressure. Pressure is a “clean” variable that can bring about large changes in structure and properties without altering the chemical composition. This makes high-pressure states amenable to computational study. We show that applying pressure shifts the SRT temperatures upward, at a rate of $\sim 17$ K/GPa. We complement the experimental measurements with finite temperature density-functional theory (DFT) calculations which also find the SRT temperatures increase with pressure, at a rate of 12 K/GPa. The calculations show how both the Nd and Co sublattice anisotropies are reduced as a result of applying pressure, but that relatively the decrease is stronger for Co, raising the SRT temperatures.

The measurements were performed on a single crystal of NdCo$_5$ grown using the optical floating zone technique. This compound has previously been prepared in different forms using other techniques. A crystal of NdCo$_5$ with a volume of $\sim 0.05$ mm$^3$ was taken from the same batch used for our recent torque magnetometry study. The crystal was loaded into a cylindrical PTFE sample holder filled with a pressure transmitting medium (Daphne oil) and placed in an easyLab Mcell 10 berylliumcopper piston clamp pressure cell. Care was taken to ensure the sample would not move in a magnetic field. Hydrostatic pressure was applied at room temperature. The pressure in the cell was determined in situ from the superconducting transition temperature in a magnetic field of 1 mT of a small piece of high purity (99.9999%) tin placed alongside the sample. Measurements were carried out between 5 and 320 K. The pressure set at room temperature varies by less than 10% over this temperature range. Magnetization measurements as a function of temperature were carried out using a Quantum Design Magnetic Property Measurement System magnetometer.

The strain- and temperature-dependent MCA of NdCo$_5$ were calculated using the theory introduced in Ref. 31. The $R$-$4f$ electrons were treated within single-ion crystal field (CF) theory, where the CF coefficients were calculated from first principles using DFT. The Co moments were treated within the disordered local moment formulation of DFT (DFT-DLM), which takes into account the reduction of magnetic order as the temperature is increased. DFT-DLM calculations were also used to parameterize the exchange field entering the CF Hamiltonian, using the scheme introduced in Ref. 8. The same computational setup was used as in previous works, using the GPaw and Fleur+ codes. The easy direction of magnetization was calculated as a function of temperature and lattice parameters, where the experimental values of $a_0 = 5.0055$ Å and $c_0 = 3.9775$ Å as reported in Ref. 36 were used to define the zero-strain structure. Uniform compressive strains of 0.5, 1.0 and 2.0% were applied, where for instance a 1% compressive strain corresponds to lattice parameters $a = 0.99a_0$, $c = 0.99c_0$.

Figure 1(a) displays the temperature dependence of the magnetization, $M(T)$, for a NdCo$_5$ crystal at various pressures. These data were collected while warming the sample at a rate of 1 K/min in an applied field, $\mu_0H = 0.05$ T. The SRT appears as a broad hump identifiable in all the $M(T)$ curves. The SRTs clearly shift to progressively higher temperatures as the applied pressure is increased up to 0.8 GPa, which is the maximum attainable with the current setup. In principle, torque magnetometry provides the clearest identification of temperatures of the SRTs, but unlike DC magnetization measurements, torque magnetometry cannot be performed inside a pressure cell. Instead, to obtain a precise location for $T_{SR1}$ and $T_{SR2}$, we show in Fig. 1(b) the first and second derivatives of $M(T)$ at ambient pressure. These data were collected while warming the sample up to 320 K. The pressure in the cell was determined in situ from the intersection of the dashed lines there is a marked increase in $dM/dT$. This temperature nearly agrees with the $T_{SR1}$ (left asterisk) obtained from our torque measurements as well as from the reported magnetization data. The zero-crossing in $dM/dT$ corresponds to the temperature ($T_{peak}$) where the $M(T)$ is maximum, but there is no clear feature in $dM/dT$ to identify $T_{SR2}$. However, plotting the second derivative reveals a dip in $d^2M/dT^2$ which lies just above the $T_{SR2}$ (right asterisk) obtained from our torque study and the reported data. We use these two features — the rise in $dM/dT$ and the minimum in $d^2M/dT^2$ — as signatures of the SRTs. The two characteristic temperatures ($T_{SR1}$ and $T_{SR2}$) identified at ambient pressure agree fairly well with our torque study which involved a different protocol of mea-
agrees with the experimental value of the calculated $\Delta V/S$ vs $P$ curve of YCo$_5$ than relying on DFT-calculated elastic properties, we use the calculated $T_{\text{SR1}}$ at significantly larger pressures than those used experimentally, but applied strain into pressure, of $6.3 \text{ GPa per } 1\% \text{ strain}$. Clearly, the calculated dependence is not linear, which could be a real effect or more likely numerical noise.

Figure 3(a) displays the experimentally measured variation with pressure of $T_{\text{SR1}}$, $T_{\text{SR2}}$, and $T_{\text{SR2}}$. For reference, $T_{\text{SR1}}$ and $T_{\text{SR2}}$ identified from previous studies$^{15,16}$ at ambient pressure are also shown in Fig. 3(a). Both $T_{\text{SR1}}$ and $T_{\text{SR2}}$ exhibit same pressure dependence of $(17 \pm 3) \text{ K/GPa}$. In Fig. 3(b) we show the calculated $T_{\text{SR2}}$ values as a function of pressure. Rather than relying on DFT-calculated elastic properties, we use the experimentally measured volume vs pressure curve of YCo$_5$ reported in Ref. 37 to perform an approximate conversion of applied strain into pressure, of $6.3 \text{ GPa per } 1\% \text{ strain}$. Clearly, the strains investigated computationally correspond to significantly larger pressures than those used experimentally, but smaller strains are more prone to numerical noise. A linear fit of the calculated $T_{\text{SR2}}$ values gives $12 \text{ K/GPa}$, in reasonable agreement with the experimental value of $(17 \pm 3) \text{ K/GPa}$.

To explain the increase in the SRT temperatures with pressure, in Fig. 4 we plot the calculated strain dependence of the leading CF coefficient $A_{20}(r^2)$ and the zero temperature anisotropy constant associated with the itinerant electrons, $K_1$. These quantities provide the main contribution to the MCA associated with the Nd and Co sublattices, respectively. Both quantities decrease in magnitude as a compressive strain is applied, showing that the MCA's of both sublattices decrease with pressure. Indeed, we verified experimentally that $K_1$ decreases with pressure by performing magnetization measurements on YCo$_5$, which, as Y is nonmagnetic, allows $K_1$ to be isolated. However, the aspect that is crucial to the SRTs is that the relative decrease with pressure is faster for $K_1$ than $A_{20}(r^2)$. This behavior is shown in the inset of Fig. 4 where the quantities have been normalized to their zero pressure values. For instance at $2\%$ strain, $K_1$ has reduced by $42\%$ compared to $A_{20}(r^2)$, which has only reduced by $17\%$. The increase in relative strength of the Nd MCA with pressure favors planar anisotropy over a wider temperature range, raising $T_{\text{SR1}}$ and $T_{\text{SR2}}$.

In conclusion, both DC magnetization experiments and DFT-DLM-based calculations have found the SRT temperatures of NdCo$_5$ increase with pressure. Furthermore, both methods find the rate of increase to be large, at $(17 \pm 3) \text{ K/GPa}$ and $12 \text{ K/GPa}$ respectively. We note that 1 GPa of applied pressure is sufficient to raise the cone–$c$-axis SRT — which coincides with the optimum temperature for a magnetocaloric cycle$^{20}$ — to room temperature. The calculations explain the pressure dependence of the SRTs, with a faster decrease in the uniaxial magnetocrystalline anisotropy associated with the Co magnetic sublattice compared to the planar Nd contribution with increasing pressure. Our work demonstrates that the application of pressure may be used to modify the temperatures of the SRTs in both NdCo$_5$ and other members of the RCo$_5$ series in a controlled way. The observation that the magnetic phase is extremely sensitive to pressure should also motivate further study of NdCo$_5$ as a potential barocaloric material. $^{38}$

See the supplementary material for details of magnetization measurements performed under pressure on a single crystal of YCo$_5$ that show $K_1$ in YCo$_5$ decreases with pressure.
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FIG. 4. Pressure dependence of (a) crystal field coefficients, $A_{20} \langle r^2 \rangle$, calculated for the Nd sublattice and (b) the zero temperature anisotropy constants, $K_1$ of Co.
