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REPORT



Exotic hysteresis of ferrimagnetic transition in Laves compound TbCo_2

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ABSTRACT

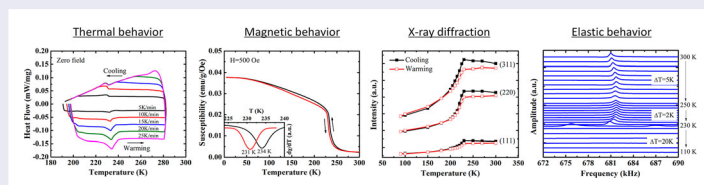
We observed exotic hysteresis behavior in the ferrimagnetic transition of a Laves compound TbCo_2 . While positive thermal hysteresis was observed in zero-field calorimetric measurements, inverse thermal hysteresis was observed in thermomagnetic measurements as a rare phenomenon. These observations confirmed a first order of the ferrimagnetic transition and revealed a lowering of this order by an external magnetic field. Elastic measurements and high-resolution synchrotron X-ray diffraction measurements suggested that the rare inverse thermal hysteresis can be related to microscopic lattice strains. Those strains are induced by a spontaneous magnetoelastic coupling and are modified by the external magnetic field.

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KEYWORDS

Laves compound; inverse thermal hysteresis; magnetoelastic coupling



IMPACT STATEMENT

This work has reconciled discrepancies about the order of the ferrimagnetic transition of a Laves compound TbCo_2 by observations of field-dependent thermal hysteresis, including rare inverse thermal hysteresis.

1. Introduction

Cubic Laves compounds of RCO_2 (R = rare earth) have shown useful properties such as large magnetostriction, large magnetoresistance and a sizeable magnetocaloric effect [1–4]. These properties are closely related to their magnetic transitions, which can be driven by a change of temperature, pressure or magnetic field [5,6]. In their magnetically ordered lattices, 4f moments of light R favor a ferromagnetic coupling with 3d moments of Co, whereas those of heavy R favor an antiferromagnetic coupling [7,8]. For this difference, the Laves compounds of heavy R show a ferrimagnetic transition in contrast to a ferromagnetic transition of the Laves compounds of light R . The ferrimagnetic transition is coupled with a tetragonal or a rhombohedral-type structural

transition and often show a first order [9]. The order of the ferrimagnetic transition of TbCo_2 has been under active debate [6,9,10–15]. While measurements of physical properties suggested a second order [9,11–13], observations of a rhombohedral-type lattice distortion near the Curie temperature T_C of ~ 230 K gave a hint at a first order [14–16]. The first order nature was also suggested by a band structure calculation of the ground-state magnetism [9] and observations of a phase coexistence around the T_C [15]. In this Letter, we report reconciliation of such discrepancies by observations of a lowering of the order of the ferrimagnetic transition by an external magnetic field. Beyond this reconciliation, we show the first observation of inverse thermal hysteresis, which is rare for a phase transition of single-phase material.

2. Experimental

Ingots of TbCo_2 were prepared by arc-melting elemental materials of Tb (99.9% purity) and Co (99.99% purity). An excess mass of $\sim 5\%$ was added for Tb to compensate for mass losses during melting. The ingots were sealed in a quartz tube and annealed at 1073 K for 168 h. The annealed ingots were cut into small pieces, otherwise crushed into powders, for different measurements. First, calorimetric measurements were carried out using a Q100 differential scanning calorimetric (DSC) device. The sample was placed in an aluminum container and swept at rates ranging from 0.5 to 25 K/min. In a few measurements, the sample was swept in a low magnetic field of ~ 50 Oe. This field was offered by an NdFeB magnet placed close to the sample. Thermomagnetic measurements were carried out using a vibrating sample magnetometer fixed in a superconducting quantum interference device in d.c. magnetic fields of 50–2000 Oe. The samples were swept at rates ranging between 5 and 15 K/min. T_C values of the samples were determined in terms of negative maxima of temperature derivative of measured dc magnetic susceptibility with an accuracy of ± 0.5 K. High-resolution X-ray diffraction (HRXRD) measurements were carried out on a powder sample in the temperature range 90–300 K using monochromatized X-rays of a wavelength of $0.4127 \text{ \AA}$ at the beamline 11-BM-B of Advanced Photon Source, Argonne National Laboratory. The sample temperature was controlled using an Oxford Cryostream with an accuracy of ± 0.1 K. Diffraction patterns were registered using an array of single crystal detectors at a high resolution of $\Delta d/d \sim 2 \times 10^{-4}$. A measuring time of 18 min was consumed at each step of temperature. Lattice parameters of the sample were determined by Rietveld refinement of the registered patterns. Elastic measurements were carried out on a cube sample of $3.7 \times 2.5 \times 1.8 \text{ mm}^3$ using a resonant ultrasonic spectrometer (RUS) installed at the University of Tennessee, Knoxville. The sample was cooled in a step-wise manner and held at each temperature for 7 min.

3. Results

As shown in Figure 1, DSC measurements revealed positive thermal hysteresis (PTH) for the ferrimagnetic transition of TbCo_2 . However, the PTH did not decrease to zero when the thermal sweeping rate was extrapolated to a zero rate. Rather, it has a residual magnitude of 0.6 K. This residual PTH is 6 times as large as the accuracy of the measured temperature. It provided conclusive evidence for a first order transition. When the sample was swept at a rate of 0.5 K/min in a magnetic field of ~ 50 Oe, the ferrimagnetic transition was split into two

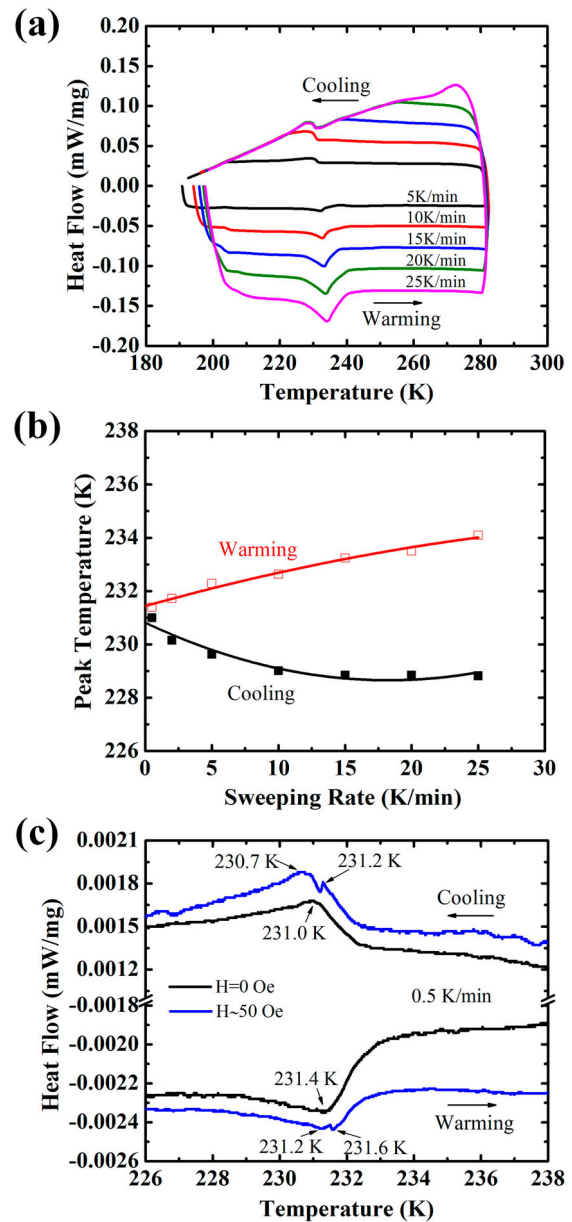


Figure 1. DSC measurements. (a) Zero-field DSC curves. (b) Dependence of peak temperatures on thermal sweeping rate. (c) DSC curves in a magnetic field of 50 Oe.

transitions. As shown in Figure 1(c), the new transitions showed zero thermal hysteresis and PTH, respectively. This splitting behavior is similar to that observed in other RCO_2 compounds at high magnetic fields [11]. However, the magnetic field applied is by two or more orders of magnitude lower. It was suggested that the ferrimagnetic transition of TbCo_2 is more sensitive to a low magnetic field.

Thermomagnetic measurements revealed inverse thermal hysteresis (ITH) for the ferrimagnetic transition. As shown in Figure 2(a), the T_C of a powder sample was determined to be 3 K lower in warming than in cooling

in a magnetic field of 500 Oe. The ITH is a rare phenomenon and has been observed in a phase-separated perovskite material only [17]. Its occurrence in a single-phase material might have a different origin. Extended measurements showed that the ITH of the sample is reproducible in a second thermomagnetic cycle and discernible at magnetic fields of up to 2000 Oe. It was evident in warming of the sample from a temperature slightly below the T_C in an opposite magnetic field of 500 Oe, suggesting that it is not sensitive to the direction of the magnetic field. Similar ITH was observed for three bulk samples (see Figure 2(b)). The ITH was not due to any technical problems because reference measurements on another ferromagnetic material in the same conditions did not reveal any kind of ITH. The ITH of the samples was found to have a relation to thermomagnetic irreversibility of magnetic susceptibility in a temperature window close to the T_C . This relation meant that it is induced by some kind of non-equilibrium magnetization kinetics. Despite its rareness, the ITH shows a strong dependence of its absolute magnitude on thermal sweeping rate like that of the PTH. As plotted in Figure 2(c), the T_C of the samples, no matter a powder or a bulk, shows opposing tendencies with declining thermal sweeping rate. As a result, the absolute magnitude of the ITH declines to zero at an extrapolated zero sweeping rate. This zero hysteresis suggested a second order ferrimagnetic transition. It meant that the order of the zero-field ferrimagnetic transition is lowered by the magnetic field applied. A similar field effect was observed for the ferrimagnetic transition of DyCo_2 [5]. For this similarity, the field-induced lowering of the order of the ferrimagnetic transition of TbCo_2 was not recognized as a rare phenomenon. Rather, it is common for the RCO_2 compound family of heavy R. For TbCo_2 , the lowering of the order by a low magnetic field is understood because the band structure calculation predicted the lowest energy barrier for its first order ferrimagnetic transition [9].

HRXRD measurements showed a decoupling of the ferrimagnetic transition from a structural transition. As shown in Figure 3(a), the (311) diffraction peak of the sample showed a backward shift at a T_C of 230 ± 2 K. This observation suggested spontaneous magnetostriction at the ferrimagnetic transition and agreed with previous observations [6,8,9,13–16]. The spontaneous magnetostriction is due to microscopic exchange interactions between Tb and Co atoms [18]. As the sign for a cubic-rhombohedral structural transition, a triple splitting of the (311) peak was not observed until the sample was cooled down to a critical temperature of $T_S = 210 \pm 2$ K. In warming, the (311) diffraction peak showed opposing changes at these critical temperatures due to reversed transitions. The T_S is 20 K lower than the T_C . This

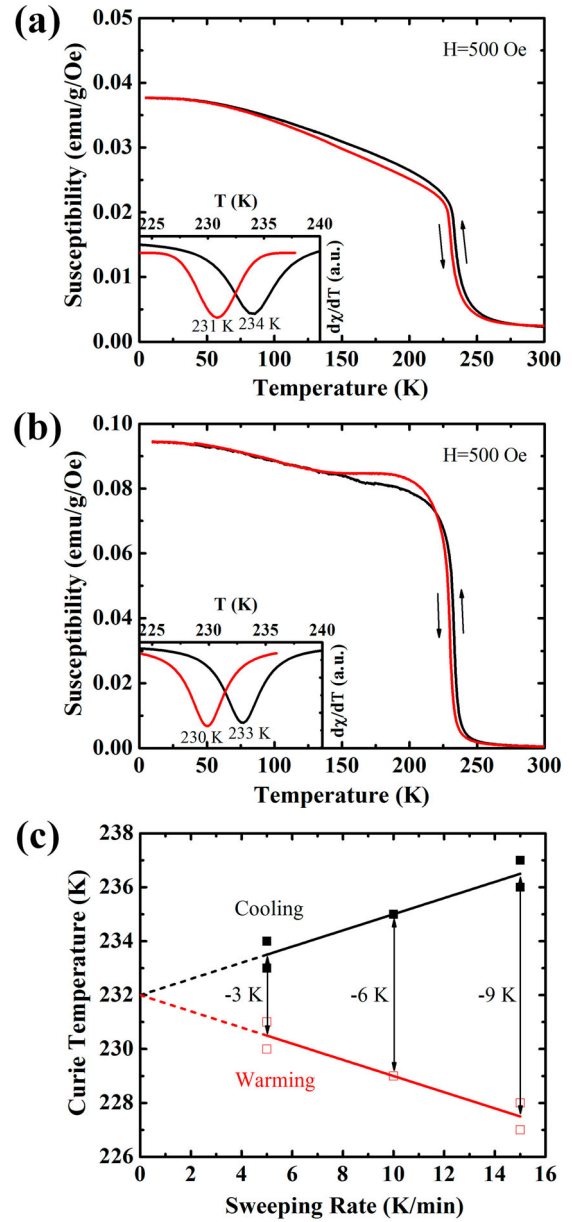


Figure 2. Thermomagnetic measurements. (a) Magnetic susceptibility χ of a powder sample. (b) Magnetic susceptibility χ of a bulk sample. (c) Curie temperatures of powder and bulk samples. Insets of (a) and (b) show temperature derivatives of magnetic susceptibility, $d\chi/dT$, for determination of Curie temperatures.

difference is 10 times as large as the temperature step of 2 K of the measurements. It provided the first evidence for a decoupling of the ferrimagnetic and the structural transition of TbCo_2 . This decoupling is neither surprising because a structural transition of GdCo_2 was observed at a temperature far below its T_C , which is higher than that of TbCo_2 [19]. Microscopically, it can be attributed to spin fluctuations of 3d electrons, which scale with temperature and may be insufficiently quenched at the ferrimagnetic transition [20]. As shown

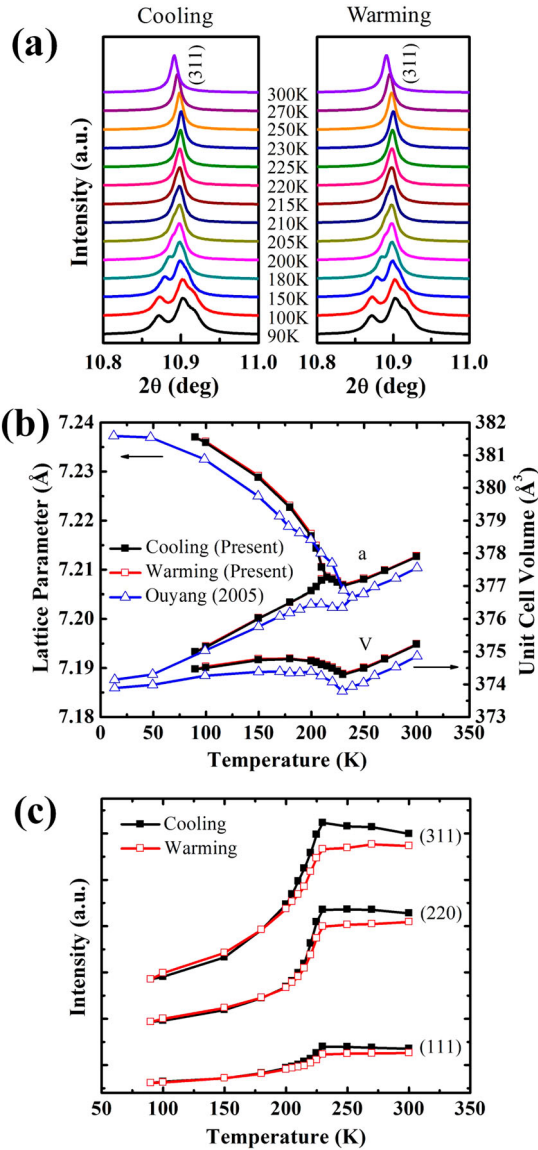


Figure 3. HRXRD measurements. (a) Profiles of the (311) diffraction peak. (b) lattice parameters and unit cell volumes (data from Ref. [14] are imposed for comparison). (c) intensities of the (311), (220) and (111) diffraction peaks.

in Figure 3(b), the lattice parameter and the unit cell volume of TbCo₂ have a discontinuous change at the T_C . This discontinuous change further confirmed the first order of its ferrimagnetic transition. The structural transition at the T_S does not bring about any discontinuous changes of lattice parameters, suggesting a second order. A similar change of the unit cell volume at the T_C has been observed in previous studies but was often interpreted as a magnetostructural transition [12–15]. Trial assumptions of a rhombohedral structure or its coexistence with the cubic structure brought about doubled or tripled residual errors of the calculated patterns and thus, were denied. The lattice parameters of the present

sample are larger than those determined by Ouyang et al. [14] using neutron powder diffraction. This systematic discrepancy can be ascribed to a difference in sample chemistry or mechanical stresses introduced in the sample preparation. However, the present data show a good agreement with other studies [12,15,16]. Especially, thermally induced lattice distortions, which were deduced from the split (440) diffraction peaks below T_C (not shown here), are in fairly good agreement with the measurement by Gignoux [16]. Diffraction intensities of the sample showed anomalies in warming. As illustrated in Figure 3(c), the (111), (220) and (311) diffraction peaks showed significant losses of intensities in warming. While the losses of the intensities reach their maxima at the T_C , they are reduced more sluggishly at the higher temperature side. Losses of the neutron diffraction intensity of the (111) peak were observed by Ouyang et al. [14] but was not interpreted. Because the mean thermal sweeping rate of the present sample is as low as 0.33 K/min, thermal stresses accumulated in cooling are supposed to be small. Then the losses of the diffraction intensities can be attributed to microscopic lattice strains.

A sharp lattice softening of TbCo₂ was observed at its ferrimagnetic transition in an earlier study [21]. The softening can be related to exchange interactions between Tb and Co atoms in a magnetically ordered state [18]. It was shown recently that the interatomic exchange interactions are preserved on a unit cell scale above the T_C , though they do not bring any short range magnetic order [20]. Then it was supposed that the lattice softening may also occur above the T_C . This hypothesis was verified by the RUS measurements. As shown in Figure 4(a), a peak of resonant frequency showed a continuous shift with decreasing temperature. The shift of the resonant frequency is swift when the T_C of the sample is approached. These changes of resonant frequency are similar to those observed in other RCo₂ compounds [22] and should have the same origin. The elastic moduli of the sample were determined from the measured peak frequencies using a standard method [23]. The Young's modulus E and shear modulus G of the sample have a value of 71.20 and 26.76 GPa, respectively at room temperature. Such values are in good agreement with the literature data [21]. Their temperature dependence verified the lattice softening above the T_C , which was not resolved in the previous study. As shown in Figure 4(b), the lattice softening sets in at a temperature of 270 K. It becomes more and more pronounced with declining temperature. This pre-transition softening of the paramagnetic lattice can account for the losses of X-ray diffraction intensities above the T_C .

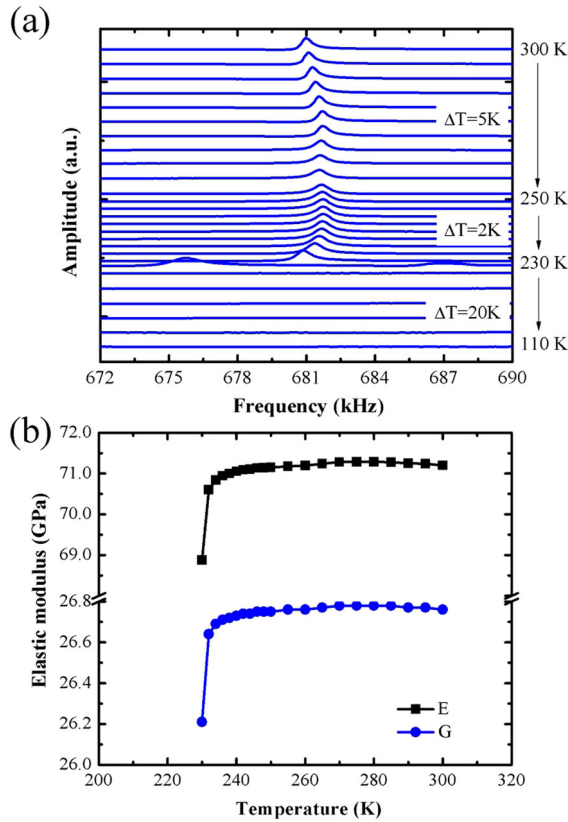


Figure 4. RUS measurements. (a) Illustration of resonant ultrasound peaks in the frequency range of 670–690 kHz. (b) Temperature dependence of the Young's modulus E and shear modulus G above the T_C .

4. Discussion

The present and earlier elastic measurements [21] allow us to explain the ITH of the ferrimagnetic transition qualitatively. First, the lattice softening above the T_C suggested the existence of microscopic lattice strains in the paramagnetic lattice of TbCo_2 due to extended magnetoelastic coupling above the T_C . When a magnetic field is applied in cooling, it may bring about local alignment of 4f moments of Tb atoms, which are stronger than 3d moments of Co atoms [13]. This alignment can break down a balance between the exchange interaction energy and the lattice strain energy in the zero-field condition and brings about magnetostriction of the paramagnetic lattice [24] via a local magnetoelastic coupling. While magnetic relaxation usually has fast kinetics, strain relaxation has much sluggish kinetics. For this difference in kinetics, neither lattice strains nor magnetization of the paramagnetic lattice could reach an equilibrium in rapid cooling. As a result, the ferrimagnetic transition has to occur under a non-equilibrium condition. In warming, the unrelaxed strain energy provides an excess driving force for ruining of a long-range ferrimagnetic order

leading to a lower T_C and therefore the ITH. This hypothesis is consistent with observations of thermomagnetic irreversibility of the present samples over a wide range of temperature (see Figure 2). The internal stress in the bulk samples may play a role. This role was hinted at by observations of a modified thermomagnetic behavior in cooling and warming. We now consider a critical energy level that is required for producing the ITH. In terms of a 20.2% modulus softening [21] and a spontaneous lattice expansion of 2.3×10^{-3} [16] at the ferrimagnetic transition, the magnetoelastic energy stored in a ferrimagnetic lattice is estimated to have a magnitude of 1.41×10^{-22} J. This value is by an order of magnitude larger than a minimum thermal energy of 1.38×10^{-23} J for producing ITH of -1 K at a hypothesized thermal sweeping rate of 1.6 K/min. Thus, the stored magnetoelastic energy is large enough to provide an energy source for the inducement of the ITH in field warming. At a high thermal sweeping rate, a thermal stress may be developed due to a thermal gradient inside the samples in field cooling. Then the stored lattice strain energy may be increased leading to more significant ITH. Because of a similar ferrimagnetic structure at low temperatures, the ITH is supposed to also occur in other RCO_2 compounds of heavy R. Extended measurements are required to confirm this speculation. From a technological point of view, the low field-induced ITH may find applications in advanced magnetic refrigerator and smart devices for energy harvest or conversion with high efficiency.

5. Conclusions

In summary, positive and inverse thermal hysteresis have been observed for the ferrimagnetic transition of TbCo_2 . These observations have suggested a field-induced lowering of the order of the ferrimagnetic transition and thus, have reconciled discrepancies in literature. As a rare phenomenon, the inverse thermal hysteresis has been attributed to a magnetoelastic strain energy, which is stored via a lattice softening at and above the Curie temperature. This rare phenomenon may also occur in other RCO_2 compounds of heavy R and requires further studies. A decoupling of the ferrimagnetic transition from a structural transition in TbCo_2 has also been observed.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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