Exchange bias-like effect in TbFeAl induced by atomic disorder

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Abstract – The exchange bias-like effect observed in the intermetallic compound TbFeAl, which displays a magnetic phase transition at \( T_h \approx 198 \) K and a second one at \( T_l \approx 154 \) K, is reported. Jump-like features are observed in the isothermal magnetization, \( M(H) \), at 2 K which disappear above 8 K. The field-cooled magnetization isotherms below 10 K show loop shifts that are reminiscent of exchange bias, also supported by the training effect. A significant coercive field, \( H_c \approx 1.5 \) T at 2 K, is observed in TbFeAl which, after an initial increase, shows a subsequent decrease with temperature. The exchange bias field, \( H_{eb} \), shows a slight increase and a subsequent leveling off with temperature. It is argued that the inherent crystallographic disorder among Fe and Al and the high magnetocrystalline anisotropy related to Tb\(^{3+}\) lead to the exchange bias effect. TbFeAl has been recently reported to show the magnetocaloric effect and the present discovery of exchange bias makes this compound a multifunctional one. The result obtained on TbFeAl generalizes the observation of exchange bias in crystallographically disordered materials and gives impetus for the search for materials with exchange bias induced by atomic disorder.

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Reviews on exchange bias [1–4] in materials point toward the importance of this effect in read-heads in magnetic recording [5], giant magnetoresistive random access memory devices [6] and in permanent magnets [7]. Interpreted as phenomena occurring at the interface between magnetically ordered microscopic regions, exchange bias interfaces can be ferromagnetic/antiferromagnetic or ferromagnetic/antiferromagnetic/spin-glass. Mixed magnetic interactions are deemed to be an important ingredient for this effect to occur. Recent work [8] promotes the importance of ferromagnetic spin structure in exchange bias and explains some of the anomalous features of the exchange bias field. In this letter we report on the observation of the exchange bias-like effect in TbFeAl. \( RFeAl \) (\( R = \) rare earth) were first investigated by Oesterreicher [9–11]. Only the heavier rare earths were observed to form the stable MgZn\(_2\)-type structure. TbFeAl has been recently identified as a magnetocaloric material [12] (albeit, a weak effect) which becomes a possible “multifunctional” compound with the observation of exchange bias.

As noted above, TbFeAl crystallizes in a hexagonal MgZn\(_2\)-type crystal structure with \( P6_3/mmc \) space group. Tb occupies the 4\( f \) Wyckoff position, while Fe and Al are situated at the 2\( a \) and 6\( h \) sites, respectively [10,11]. Mixed occupation of Fe and Al is possible in this structure. Magnetically, TbFeAl is a ferrimagnet with a transition temperature of 195 K [12]. A saturation-like effect of magnetization which displayed an \( S \)-curve was observed [9] which was described as a consequence of partial chemical disorder of Fe and Al. Significantly high magnetocrystalline anisotropy leading to the formation of thin domain walls which are pinned to defects influences the magnetization, and to some extent, is the reason for the magnetocaloric effect [12].

Partial or total crystallographic disorder is a favourable ingredient for the observation of exchange bias. Granular nanoparticles in a structurally and magnetically disordered matrix [13] or interacting magnetic defects
Harikrishnan S. Nair and André M. Strydom

Fig. 1: (Colour online) Top: the powder x-ray diffraction pattern of TbFeAl along with the Rietveld refinement. The black circles are the experimentally observed intensity, the red solid line is the calculated intensity assuming $P6_3/mmc$ space group. The difference curve is shown as green solid line and the allowed Bragg peaks as vertical bars. Bottom: the hexagonal framework of TbFeAl shown as a projection onto the $ab$-plane.

Fig. 2: (Colour online) Magnetization curves (ZFC and FC) of TbFeAl obtained at 200 Oe. Two magnetic transitions at $T_h^c \approx 198$ K and $T_l^c \approx 154$ K are observed. The inset (a) shows the derivative plot, $dM/dT$, used to determine the transition temperatures. The inset (b) magnifies the region close to 250 K ($> T_h^c$) where a “loop”-like feature is seen.

embedded in an antiferromagnetic matrix with high degree of disorder [14] are example systems where disorder brings about the exchange bias effect. In the oxide $Y_2CoMnO_6$, below 8 K prominent steps in magnetization and significant coercive field of $\approx 2$ T were observed [15]. Martensitic-like growth of ferromagnetic domains, formed as a result of antisite disorder, was postulated as the reason for exchange bias in $Y_2CoMnO_6$. Motivated by the prospect of obtaining a general feature of exchange bias induced by disorder, we have extended our research to a disordered intermetallic compound TbFeAl.

The polycrystalline sample used in this study was prepared using the arc melting method. The elements Tb, Fe and Al (all 4N purity) were melted in the water-cooled Cu hearth of an Edmund Buehler furnace in argon atmosphere. The once-melted buttons were remelted four or five times to ensure homogeneity. Post melting, powder x-ray diffractograms were recorded on pulverized samples in a Rigaku SmartLab x-ray diffractometer which used Cu $K\alpha$ radiation. Magnetic properties were recorded using a Magnetic Property Measurement System from Quantum Design Inc., San Diego. Magnetization as a function of temperature in the range 2–350 K in both zero-field–cooled (ZFC) and field-cooled (FC) protocols as well as magnetic field in the range 0–7 T and ac susceptibility measurements were performed.

The experimentally obtained powder x-ray diffractogram is presented in fig. 1 as black circles. The observed peaks could be indexed in the hexagonal space group $P6_3/mmc$ (MgZn$_2$ type). The FullProf suite of programs [16] was used to perform a Rietveld analysis [17] of the x-ray data which yielded $a$ (Å) = 5.3975(4) and $c$ (Å) = 8.7526(3). The results of the Rietveld refinement are presented in fig. 1. In the bottom panel of fig. 1, the hexagonal structure of TbFeAl is shown as a projection on to the $ab$ plane.

The magnetic phase transitions reported in the literature for TbFeAl [12,18,19] are reproduced in the magnetization curve, $M(T)$, obtained at 200 Oe which is presented in fig. 2. A bifurcation between the ZFC and FC arms is observed at $\approx 275$ K (see inset (b)) followed by two humps at 186 K and at 145 K. The transition temperatures are determined by taking the derivative of $M(T)$ and is plotted as $dM/dT$ in the inset (a). From this, $T_h^c \approx 198$ K and $T_l^c \approx 154$ K are determined. In the literature, the second transition is attributed to the existence of two crystallographic regions in the sample with different occupation of Fe and Al on the sites 2$a$ and 6$h$. The FC arm of $M(T)$ suggests that upon application of a magnetic field, ferromagnetic-like enhancement of magnetization occurs. In the inset (b) of fig. 2, the high-temperature region of $M(T)$ for $T \geq T_h^b$ is shown magnified to highlight a “loop”-like structure. It is to be noted that no significant linear region is observed up to 350 K and hence a description of magnetic susceptibility following the ideal Curie-Weiss formalism does not hold. The “loop”-like structure in $M(T)$ at high temperature might suggest the presence of magnetic correlations extending above $T_h^c$.

The ferromagnetic feature of TbFeAl is evident from the isothermal magnetization curve, $M(H)$, at 5 K and 10 K.
Exchange bias-like effect in TbFeAl induced by atomic disorder

Fig. 3: (Colour online) (a) Isothermal magnetization curves, $M(H)$, in the zero-field–cooled mode for TbFeAl measured at 5 K and 10 K. At 10 K, no jumps in magnetization are visible while at 5 K they are present. A significant coercive field is observed in both cases and the saturation magnetization attains $\approx 5.8 \, \mu_B$/f.u. (b) The magnetization isotherms at 2 K obtained under different values of field cooling. The ZFC curve is also plotted for a comparison. (c) The magnetization isotherms at 4, 6, 8 and 10 K after field cooling in 1000 Oe from 300 K. The field-cooled curves display clear evidence for loop shifts reminiscent of the exchange bias effect.

Figures 4(a), (b) present the evolution of $H_c$ and $H_{eb}$ as a function of temperature. Though TbFeAl displays significant $H_c$ (about 1.5 T at 6 K), it is lower than that of Y$_2$CoMnO$_6$ which has similar domain-related structure [15]. Generally, a monotonous decrease of $H_c$ with increasing temperature is favoured. However, disordered granular systems are reported to show a variation of $H_c$ similar to what has been observed for TbFeAl [13]. The anomalous temperature dependence of $H_{eb}$ could be related to the recent work on the role of ferromagnetic layers or domains in exchange bias [8] where, contrary to the conventional case, an increase of $H_{eb}$ with temperature is explained. The atomic disorder in TbFeAl could be held responsible for such a behaviour. Interestingly, though the
$H_c$ of TbFeAl shows an initial increase and subsequent decrease with temperature, $H_{hyst}$ increases first and attains a near-constant value up to 15 K.

The exchange bias effect results from interfaces between ferromagnetic, antiferromagnetic or spin-glass regions. In order to probe the presence of spin glass in TbFeAl, ac susceptibility measurements were carried out at frequencies ranging from 0.1 Hz to 999 Hz. The results are presented in fig. 4(c). The susceptibility peaks at $T^c_1$ and $T^c_2$ are observed to show no frequency dependence other than weak damping. The peak positions were determined by taking the derivative $d\chi'(f, T)/dT$. It is then clear that the disorder in this material only pertains to structural aspects. It was not possible to quantify the degree of disorder related to the mixed occupancy between Fe and Al from the x-ray data. However, with the introduction of the mixed occupancy, an improvement in the goodness-of-fit of refinement was observed. The presence of nano-scaled magnetic domains in RFeAl was experimentally observed in the case of TmFeAl [20] where the crystallographic disorder and the high magnetocrystalline anisotropy of Tm were the reason for this. By comparison, the experimental data presented here for TbFeAl suggests a similar scenario. Finally, the loop shifts observed in the training effect experiment presented in fig. 5 confirms the exchange bias in TbFeAl. Hysteresis loops were measured at 2 K for 4 continuous loops after field cooling the sample using 1000 Oe. It can be seen that the hysteresis curves begin to shift with increasing number of loops. For clarity, only a part of the hysteresis is shown in (a). A fully magnified view of the loop shift is provided in (b). We now employ a similar training effect experiment presented in fig. 5 confirms the exchange bias in ferromagnetic TbFeAl with significant coercive field. $H_c$ is observed at 2 K. Magnetic saturation is observed in isothermal magnetization curves below 5 K, however, not reaching the full ferromagnetic moment of Tb$^{3+}$. The crystallographic disorder among the Fe-Al sublattice and the strong magnetocrystalline anisotropy of Tb$^{3+}$ are argued to be the reason for the observed domain effects that lead to exchange bias. The results presented in this work attains a general feature following the extension from the exchange bias effect observed in double perovskite Y$_2$CoMnO$_6$ which was driven by the theme exchange bias-induced by atomic disorder.

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