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Successive magnetic transitions in $TbNiAl_2$ studied by neutron diffraction

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Abstract. We report measurements of DC (AC) magnetic susceptibility and neutron diffraction on $TbNiAl_2$ alloy. The Rietveld refinements of the x-ray and neutron diffraction data are consistent with an orthorhombic structure of the type $MgCuAl_2$ (space group *Cmcm*). The results of DC (AC)- magnetic susceptibility show two successive magnetic transitions at 20 K and 11.7 K with antiferromagnetic and ferromagnetic (or ferrimagnetic) features, respectively. On the other hand, neutron diffraction patterns show that, below 20 K and down to 12 K, new reflexions appear, confirming the antiferromagnetic character of the transition observed in the macroscopic measurements. Also, at least one of these new reflexions, located at Q = 1.2 $Å^{-1}$, shifts to higher angles when the temperature decreases, indicating an incommensurate magnetic structure. Below 11 K, many reflexions disappear and new reflexions increase, evidencing a new magnetic transition.

1. Introduction

Tb intermetallic compounds have been extensively studied from both fundamental and applied points of view because their exotic magnetic behaviours and the interesting properties they show, associated for instance, with the magnetocaloric effect [1]. In particular, Tb alloys within the Tb-Ni-Al phase diagram present several magnetic transitions, which have been exhaustively studied. For instance, in TbNiAl two Tb sites out of three per unit cell order with a Neel temperature of T_N =47 K, while the third site is frustrated and contributes to a second magnetic phase transition at 23 K [2]. The magnetic structure of this alloy was determined by neutron diffraction [3]. Also, the maximum entropy change and refrigerant capacity obtained by means of thermal and magnetic properties are 13.8 $Jkg^{-1}K^{-1}$ near T_N and 494 Jkg^{-1} respectively for a magnetic field change of 50 kOe [4], values comparable to that observed in Gd.

On the other hand, in $TbNiAl_4$ antiferromagnetic (AFM) transitions, in zero applied magnetic field, were observed at 28 and 34 K. The magnetic structure of the lowest temperature phase is AFM with a *(0 1 0)* propagation vector, as obtained from neutron diffraction [5]. The magnetocaloric properties of single crystals also revealed interesting features with a large inverse entropy change associated with a field-induced step-like magnetic behaviour, and probably due to a transition from a commensurate AFM phase to incommensurate magnetic phase [6].

$TbNiAl_2$ is another ternary alloy of the Tb-Ni-Al diagram which is known to crystallize in orthorhombic $MgCuAl_2$- type of structure, and with a paramagnetic behaviour above 80 K [7]. However, details of the low temperature properties have not been reported yet. In the present work, we will provide a more detailed description of the magnetic properties of this alloy by DC and AC-susceptibility measurements, and by neutron diffraction.

2. Experimental details

A polycrystalline $TbNiAl_2$ alloy was prepared in an arc furnace from stoichiometric amounts of Tb (3N Alfa), Ni (5N, Alfa) and Al (5N, Alfa) metals. X-ray diffraction measurements were carried out in a Brucker diffractometer with CuK_α radiation. AC (DC) magnetic susceptibility measurements were collected in a Quantum Design PPMS in the temperature range 2 - 300 K and magnetic fields up to 9 T. Neutron diffraction measurements were recorded at the D1B and D1A beamlines, at the high flux reactor of the Institute Laue Langevin (ILL)-Grenoble.

3. Results and Discussion

Rietveld refinements of X-ray powder diffraction experimental data are consistent with an orthorhombic $MgCuAl_2$-type structure, space group *Cmcm*, and lattice parameters a = 4.042(1) Å, b = 10.263(1) Å and c = 6.893(2) Å, in good agreement with those reported in the literature [7].

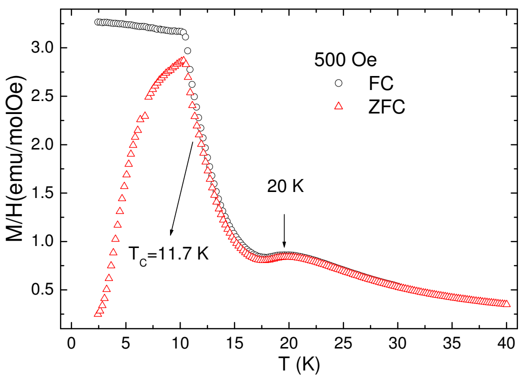

Figure 1. Temperature dependence of ZFC-FC curves of DC-magnetic susceptibility at 500 Oe.

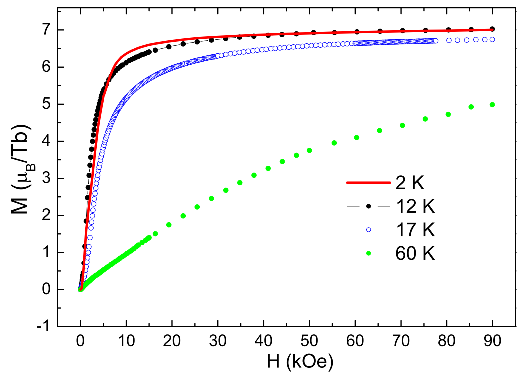

Figure 2. Field dependence of the isothermal magnetization curves at 2, 12, 17 and 60 K for $TbNiAl_2$ alloy.

The temperature dependence of zero field cooled (ZFC) and field cooled (FC) DC-magnetic susceptibility (χ=M/H) curves at 500 Oe is shown in Figure 1. At 20 K, the ZFC and FC curves present a small peak, and come together into one single curve, suggesting an AFM behaviour. At lower temperatures, below 12 K, the FC curve saturates on going to lower temperatures, which resembles a ferromagnetic (FM) behaviour. From the inflexion point of these curves, an ordering temperature of 11.7 K is estimated. The presence of a maximum in the ZFC curve (around 10 K), and a large irreversibility, point towards the existence of FM-like domains in this material. In the high temperature region (above 50 K), a Curie-Weiss behaviour is found, with μ_{eff} = 9.37 μ_B, value near to the free ion Tb^{3+} (9.72 μ_B), and a negative paramagnetic Curie temperature (θ_p=-6 K) suggesting the presence of AFM interactions. Also, the field dependence of the isothermal magnetization at 2, 12 K and 17 K (see Figure 2), shows a full saturation at the highest achieved magnetic field of 90 kOe, with values of 7.02 μ_B (2 and 12 K) and 6.75 μ_B (17 K) still far from the expected gJ value of 9 μ_B for the full multiplet of Tb^{3+} (g=3/2, J=6), which could be attributed to crystalline field effects.

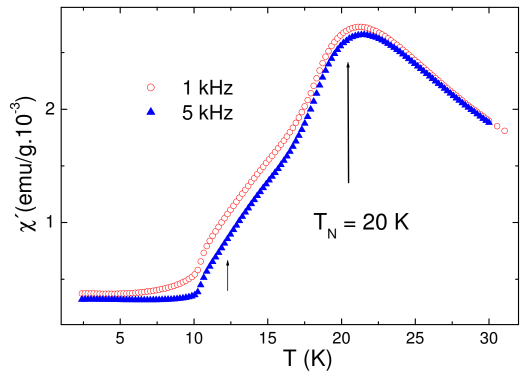

Figure 3. Temperature dependence of the real component (χ') of the AC-magnetic susceptibility at 1 and 5 kHz.

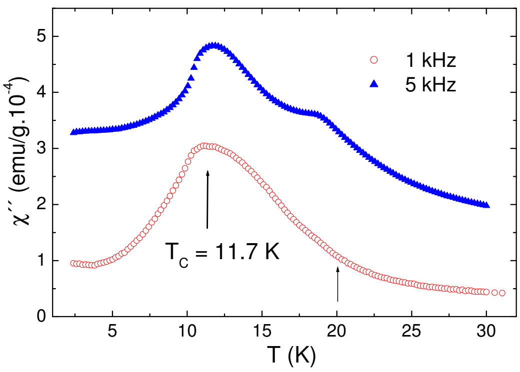

Figure 4. Imaginary component (χ'') vs T of the AC-magnetic susceptibility at 1 and 5 kHz.

Measurements of the AC-susceptibility also could provide an useful information about the magnetic transitions. In this sense, the temperature dependence of the real (χ') and imaginary (χ'') components of the AC-susceptibility at frequencies of 1 and 5 kHz are presented in figure 3 and 4, respectively. In χ', a maximum at 20 K, and a broad anomaly centered around 12 K are observed. Moreover, in (χ''), a peak around 11.7 K appears, whereas at 20 K a second *tiny* anomaly develops for 5 kHz. As it is well known the peak in χ'' is commonly associated to dynamic processes of domain movements, whereas the increase of the absolute value of χ'' for 5 kHz can be attributed to a contribution to the susceptibility arising from currents induced in the sample by the alternating magnetic field, as observed in other intermetallic systems [8]. Therefore, the overall behaviour of the AC-magnetic susceptibility is in good agreement with the DC-magnetic susceptibility results indicating an AFM transition at 20 K and a FM (or ferrimagnetic) ordering around 11.7 K.

In figure 5, neutron diffraction patterns at different temperatures of the $TbNiAl_2$ alloy are presented. A comparison of the pattern in the paramagnetic region (30 K) with those related to the low temperature magnetic phases at 2 and 14 K, are shown in figure 5(a,b). It is observed that new peaks appear in the low temperature diffraction patterns, indicating an AFM arrangement of the magnetic moments. We could notice that at 14 K new peaks are detected up to 65° whereas at 2 K a new set of magnetic reflexions appear even up to 130°. In both magnetic phases it is observed a reduction of the background due to the decrease of the anisotropic scattering of the magnetic moments with the arising of the ordering state. An interesting feature is found at temperatures between 17.5 and 11 K, where the magnetic peak at Q = 1.2 $Å^{-1}$ shifts to higher angles when the temperature decreases, indicating an incommensurate magnetic phase (figure 5 (c)). Due to the complexity of the magnetic structures, it has not been possible to determine the appropriate magnetic propagation vectors. Although, the overall evolution of the magnetic Bragg peaks with the temperature, is consistent with the onset of the magnetic transitions, as estimated from the DC and AC-magnetic susceptibilities (figure 5 (d)).

From the above results it is evident the existence of two magnetic transitions of different nature in the $TbNiAl_2$ alloy. This situation is not uncommon as it is similar to that found in other ternary alloys as TbNiAl [2, 3, 4] and $TbNiAl_4$ [5, 6].

4. Conclusions

Summarizing, the results of DC(AC)-susceptibility and neutron diffraction on the $TbNiAl_2$ alloy are consistent with two successive magnetic transitions at T_N = 20 K and T_C= 11.7 K. The

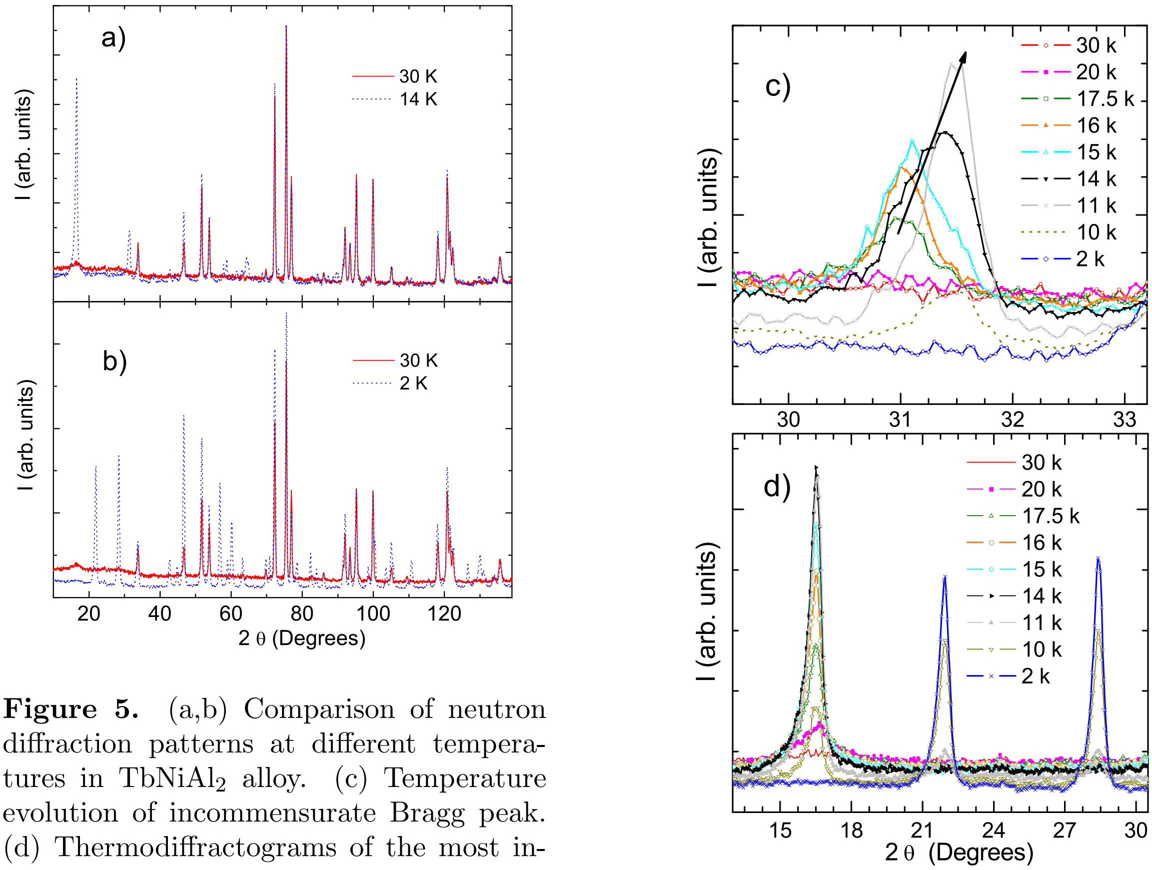

Figure 5. (a,b) Comparison of neutron diffraction patterns at different temperatures in $TbNiAl_2$ alloy. (c) Temperature evolution of incommensurate Bragg peak. (d) Thermodiffractograms of the most intense magnetic peaks.

analysis of thermodiffractograms of neutron diffraction patterns indicates an incommensurate AFM structure for the first, and very likely, a commensurate ferrimagnetic ones for the second at lower temperatures, respectively. It would be interesting to study the influence of pressure and magnetic field on the magnetic transitions of this intermetallic, as well as the magnetocaloric effect.

Acknowledgments

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