Magnetic and magnetocaloric properties of the intermetallic compound TbNiAl

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Abstract

Magnetization measurements have been carried out on the intermetallic compound TbNiAl in applied fields up to 120 kOe. Temperature dependence of magnetization under zero-field-cooled and field-cooled conditions shows thermomagnetic irreversibility, which is attributed to magnetic frustration. With the increase of field, the irreversibility decreases and vanishes completely at high fields. Magnetocaloric effect has been calculated in terms of isothermal magnetic entropy change using magnetization isotherms obtained at various temperatures. The maximum entropy change is 13.8 J kg\textsuperscript{-1} K\textsuperscript{-1} near the ordering temperature for a field change of 50 kOe. The refrigerant capacity is found to be 494 J kg\textsuperscript{-1} for the same field change and for a temperature difference of 52 K between the cold and the hot sinks.

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1. Introduction

The search for potential magnetic refrigerant materials is mainly focused towards the rare earth (R)–transition metal (TM) intermetallic compounds owing to the large magnetocaloric effect (MCE) exhibited by them near the magnetic transitions [1,2]. The use of magnetic refrigeration as an alternative to the conventional gas compression method has led to an intensive research, both on experimental as well as theoretical aspects, in the field of MCE [3–5]. Though MCE can be measured directly using calorimetric techniques, indirect calculation methods in terms of isothermal magnetic entropy change or adiabatic temperature change are more prevalent. Materials should possess considerable MCE over a span of temperature in order to be considered as practical refrigerants. In general, MCE is found to be maximum near the magnetic ordering temperature and, therefore, composite materials with distributed ordering temperatures or materials with multiple magnetic transitions are preferred for refrigeration applications [2]. In this context, RNiAl compounds, which possess a complex magnetic structure and undergo multiple magnetic transitions, are important and warrant a detailed experimental study of MCE. Though the magnetic properties of these compounds have been well studied, very little work has been reported on their magnetocaloric behavior. In the present communication, we have tried to correlate the magnetic and magnetocaloric properties of the intermetallic compound TbNiAl.

2. Experimental details

The polycrystalline sample of TbNiAl was prepared by arc melting the constituent elements (of at least 99.9\% purity) in high-purity argon atmosphere. The ingot was melted several times to ensure homogeneity and the final weight loss was less than 1\%. Lattice parameters were determined from powder X-ray diffraction (XRD) patterns using Cu K\textsubscript{α} radiation. Magnetization measurements, in
the temperature range 2–120 K and up to a maximum field of 120 kOe, were performed using a vibrating sample magnetometer (VSM, Oxford Instruments). The temperature variation of magnetization, under zero-field-cooled (ZFC) and field-cooled (FC) conditions, was measured up to a maximum field of 20 kOe. In the ZFC mode, the sample was cooled to the lowest temperature in the absence of an applied magnetic field and the magnetization was measured in a fixed magnetic field on warming. However, in the FC mode, the sample was cooled in a constant applied field, which was retained during warming to measure the magnetization. ZFC and FC curves were obtained at the same warming rate. The magnetization isotherms in the temperature range 18–74 K were used for the calculation of isothermal magnetic entropy change. These isotherms were obtained in the increasing-field mode, as the temperature was increased from 18 to 74 K. Before measuring the magnetization isotherms, the sample was heated to above the ordering temperature and then cooled to the desired temperature.

3. Results and discussion

Fig. 1 shows the Rietveld-refined room temperature powder X-ray diffractogram for TbNiAl using the Fullprof program. The fitting revealed that the compound has formed in single phase with the hexagonal ZrNiAl-type structure (space group P62m, no. 189). The lattice parameters were found to be \(a = 6.987 \pm 0.009\) and \(c = 3.869 \pm 0.005\) Å. Fig. 2 shows the temperature \((T)\) dependence of magnetization \((M)\), in various applied fields \((H)\), under ZFC and FC conditions. The \(M-T\) data show two magnetic transitions, one at 23 and the other at 48 K. Neutron diffraction measurements reported earlier in this compound [6, 7] have revealed the existence of antiferromagnetic ordering with a Neel temperature \((T_N)\) of 47 K. Therefore, the present \(M-T\) data seem to be in agreement with the neutron diffraction results. The low-temperature transition appears to be weak, as can be seen from Fig. 2.

Fig. 2. Temperature dependence of magnetization of TbNiAl under ZFC and FC conditions in various applied magnetic fields. Arrows indicate the low-temperature transition at about 23 K.

It may be noted from Fig. 2 that the magnetization data, collected in applied fields up to 2 kOe under FC and ZFC conditions, show thermo-magnetic irreversibility. Generally, the thermo-magnetic irreversibility is observed in narrow-domain wall systems or geometrically frustrated systems. It is reported that TbNiAl is a geometrically frustrated system with antiferromagnetic ordering along the \(c\)-axis as well as in the \(ab\)-plane of the hexagonal unit cell [6–8]. The Tb ions form a triangular lattice in the \(ab\)-plane, which leads to the magnetic frustration in this compound. The low-temperature peak (~23 K), observed in the \(M-T\) data, arises due to the ordering of these frustrated moments, as the temperature is lowered. Though the thermo-magnetic irreversibility and low temperature transition exist up to an applied field of 2 kOe, they seem to vanish for a field of 20 kOe. This may be due to the fact that above a critical field (less than 20 kOe), the strength of the antiferromagnetic interactions decreases, thereby reducing the effects of frustration.

Fig. 3 shows the field dependence of magnetization of TbNiAl at 2 K. The inset shows the low-field region of the \(M-H\) plot at the same temperature. As can be seen, the magnetization shows an abrupt change at about 10 kOe.
This may be due to a field-induced metamagnetic transition from an antiferromagnetic to a predominantly ferromagnetic state. It is of interest to note that this observation is consistent with the $M - T$ plots shown in Fig. 2. However, it may also be possible that this transition is a result of a crystallographic change occurring at low temperature.

From the $M - H$ data obtained at 2 K, the saturation moment is calculated to be $8.3 \mu_B$ f.u., for a maximum field of 120 kOe. Ehlers and Maletta [8] have reported that the magnetic structure of TbNiAl can be analyzed in terms of two sublattices with magnetic propagation vectors $(1/2, 1/2, 1/2)$ and $(1/2, 0, 1/2)$. Though the temperature dependences of the magnetization of these sublattices are different, the magnetization values are almost the same at 2 K. The average magnetic moment at 2 K is reported to be about $8.6 \mu_B$ f.u., which is very close to the value derived from the $M - H$ isotherm at 2 K in the present case. It has also been reported [9] that the nature of low-temperature magnetization isotherms in TbNiAl and GdNiAl are not similar to those of conventional antiferromagnets and this has prompted these authors to assume the existence of some ferromagnetic phase in both TbNiAl and GdNiAl. On the other hand, these authors also report that the low-temperature transitions in both these compounds are pushed to lower temperatures on application of magnetic fields, which is indicative of a low-temperature antiferromagnetic phase.

The remanence ratio ($M_r / M_s$) estimated from the $M - H$ plots is found to be about 7.5% at 2 K, which decreases to about 1% near $T_N$. This implies that the magnetic hardness is considerable only at low temperatures. At temperatures above $T_N$, the magnetic susceptibility obeys the Curie-Weiss law with an effective paramagnetic moment of $9.7 \mu_B$, which is equal to the free ion value of Tb$^{3+}$ ion.

Fig. 3. Field dependence of magnetization obtained at 2 K. Inset shows the low-field region of the magnetization isotherm. Arrows indicate the data corresponding to the increasing and decreasing fields.

Fig. 4a shows the field dependence of magnetization data, collected in the temperature range 18–74 K at intervals of 4 K, up to a maximum field of 50 kOe. The low-field region of the $M - H$ plots below $T_N$ is expanded and is shown in Fig. 4b. It can be seen from Fig. 4b that, below a critical field, the magnetization value at 46 K is higher than that at 18 K. However, at higher fields, this trend reverses and the low-temperature magnetization becomes larger than the high-temperature value. This indicates that the compound is antiferromagnetic below a certain field. However, it can be made ferromagnetic with the application of a suitable field. Such a transition has indeed been observed in Fig. 3. The occurrence of a field-induced metamagnetic transition resulting in a ferromagnetic state has been reported in many intermetallic compounds [10].
changes of 20 and 50 kOe (with $T_{\text{cold}} = 20$ and $T_{\text{hot}} = 72$ K) are 199 and 494 J kg$^{-1}$, respectively. It is of interest to note that the $q$ value of Gd, for a field change of 10 kOe and a temperature difference (between the cold and hot sinks) of 60 K is about 78 J kg$^{-1}$ [11]. This suggests that the refrigerant capacity in TbNiAl is comparable to that of Gd, which is used in practical magnetic refrigerators.

4. Conclusion

In conclusion, the thermomagnetic irreversibility in TbNiAl seems to arise due to magnetic frustration. With the increase in magnetic field, the frustration effect decreases, which may be attributed to a metamagnetic transition. The low-temperature magnetization behavior probably indicates the existence of some ferromagnetic component along with the antiferromagnetic character. A detailed neutron diffraction study is essential to understand the exact magnetic state, especially at low temperatures ($\sim$2 K). The magnetocaloric properties of TbNiAl are found to be comparable to those of many potential magnetic refrigerants. Furthermore, the low remanence ratio (about 1%) near $T_N$ indicates that TbNiAl is magnetically soft, which is an additional criterion for a good refrigerant material. The high values of entropy change and refrigerant capacity along with magnetic softness make the present compound a promising candidate for refrigeration applications near 50 K.

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References