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Magnetic and magnetocaloric properties of ball milled Nd₅Ge₃

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Effect of particle size reduction of the intermetallic compound Nd₅Ge₃ by ball milling has been studied by investigating the change in the magnetic and magnetocaloric properties. Ball milling is found to enhance the strength of the ferromagnetic component. An analysis based on the Arrott plots shows clear difference in the critical exponents between the bulk and the ball milled samples. Though the maximum entropy change and the relative cooling power are not altered much by the size reduction, magnetic transition temperature is affected. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3700243>]

I. INTRODUCTION

Magnetism of rare earth intermetallic compounds has been the focus for a long time because of its importance from a fundamental perspective as well as from the point of view of applications.^{1–3} One of the most significant and recent developments related to these materials is the possibility of using some of them as magnetic refrigerants for magnetic cooling applications.^{3–8} This refrigeration technology is being seriously considered as an effective alternative to the conventional gas compression/expansion technology. Magnetocaloric effect (MCE), which is the underlying physical property that determines the efficiency of a magnetic refrigerant, has become an important topic of research for the last few years, both from the fundamental and applied points of view. The MCE is an intrinsic thermodynamic property of a magnetic material and is measured in terms of magnetic entropy change (ΔS_M) on the application of a magnetic field. The materials should exhibit comparatively large MCE over a broad temperature span in order to be considered as good refrigerants for the practical applications. Hence, there is a strong demand for materials with large MCE for the successful design of a practical refrigerator. Some of the most important systems of this family are Gd₅(Ge_{1-x}Si_x)₄, La(Fe_{1-x}Si_x)₁₃, RCo₂.^{3–8} These systems possess large MCE associated with their first order magnetic transition (FOMT) from paramagnetic (PM) to ferromagnetic (FM) state. One of the biggest advantages of this class of materials is that the magnetic transition temperature and thereby the operating temperature of the refrigerant can be tuned with the help of substitutions. In addition to entropy change, the quality factor of a refrigerant is expressed in terms of relative cooling power (RCP), which is estimated as the area enclosed by the ΔS_M versus T curve between the points corresponding to the full width at half maximum. A first order magnetic transition is accompanied by a thermal and magnetic hysteresis, which reduces the relative cooling power of the refrigerant. Besides, FOMT results in MCE peaks that are very narrow in temperature span compared to the second order

phase transition. Therefore, materials with second order transition are also of interest.

Most of the reports on the magnetic as well as magnetocaloric properties of rare-earth intermetallics are on the bulk form; very little attention has been paid to the nano-particles of these materials, mainly because of the difficulty in preparing the fine particles without oxidation problem. Recently, there are few successful attempts of stabilizing rare-earth nano particles using a core-shell morphology.^{9–13} We have recently studied the magnetic properties of the intermetallic compound Nd₅Ge₃ in the bulk form and found that it shows interesting magnetic and related properties.^{14,15} The most important observation is the spontaneous magnetization jump at low temperatures, as seen in phase separated systems. The other observations are the field induced irreversibility in magnetization, electrical resistivity, and heat capacity isotherms. It was also found that the material shows re-entrant spin glass behavior at low temperatures.¹⁵ In view of these observations, we have studied the magnetic properties of this compound in the fine particle form. In this paper, we report a comparative study of the magnetic and magnetocaloric properties of the ball milled Nd₅Ge₃ and its bulk counterpart.

II. EXPERIMENTAL DETAILS

The polycrystalline sample of Nd₅Ge₃ was prepared by arc melting a stoichiometric mixture of Nd (99.9 - at. % purity) and Ge (99.999-at. % purity), in a water-cooled copper hearth, in high purity argon atmosphere. The resulting ingot was turned upside down and remelted several times to ensure homogeneity. The weight loss after the final melting was less than 0.5%. The resulting sample was subjected to high energy ball milling to get the reduced particle size. We used tungsten carbide bowls and balls to produce the powder in Ar atmosphere. The weight ratio of sample to balls was 1 : 10. The total running time was 16 h and 20 min. All processing of the powder was conducted in a glovebox under inert atmosphere. The structural analysis of the ball milled sample was performed by room temperature powder x-ray diffractogram (XRD) using Cu-K α radiation. The microstructure of the ball milled sample was examined by scanning electron microscopy (ESEM-FEI quanta 200) and high

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resolution transmission electron microscopy (JOEL, JEM 2100 F). The magnetization measurements were carried out using a vibrating sample magnetometer attached to a Physical Property Measurement System (Quantum Design, PPMS-6500).

III. RESULTS

The XRD patterns (Fig. 1) along with Rietveld refinement of the bulk and the ball milled samples show that there is no change in the crystal structure after ball milling. Sharp peaks in the XRD pattern of ball milled sample confirm that the sample is crystalline after milling. As expected, ball milling makes XRD peaks broader. The lattice parameters obtained from Rietveld refinement are almost the same for bulk and ball milled samples. The average particle size of the ball milled sample, estimated from the Scherrer formula using the width of the most intense peak, is $\sim 2 \mu\text{m}$. Figures 2(a) and 2(b) show SEM and TEM images of the ball milled sample. SEM image reveals a broad size distribution of the aggregated powder particles. TEM image indicates that the particle size is somewhat smaller than that determined from the XRD data.

Figure 3 shows the field cooled (FC) and zero field cooled (ZFC) magnetization versus temperature curves in a magnetic field of 0.5 kOe and 5 kOe for both ball milled as well as bulk Nd_5Ge_3 samples. It can be seen that the ZFC curve of the bulk sample undergoes two magnetic transitions at 30 K and 49 K. On the other hand, there is only one peak, at 41 K, for the ball-milled sample. Furthermore, the peak observed in the ZFC curve of the ball milled sample disappears in the FC curve. In a recent report, we have shown that the low temperature peak (30 K) in the bulk sample is of spin glass nature.¹⁵ Therefore, the suppression of this peak in the ball milled sample indicates enhancement of the ferromagnetic component, as compared to that in the bulk alloy. This enhancement of the ferromagnetic component is also observed in the magnetization values of the M-T curves. In the magnetically ordered region, the magnetic moment of the milled sample is much higher compared to that of the bulk alloy in the same field. This gives an indication that the anti-ferromagnetic (AFM) strength decreases with ball milling.

FIG. 1. Rietveld refined x-ray powder diffraction patterns of ball milled and bulk Nd_5Ge_3 .

FIG. 2. (a) SEM and (b) TEM images of ball milled Nd_5Ge_3 .

A similar observation was reported in the fine particles of GdMn_2Ge_2 and TbMn_2Ge_2 .¹⁶ However, an exactly opposite trend has been observed in Ni-Mn-Sn and Ni-Co-Mn-Sb alloys,^{17,18} which have some similarities with the present material. It can also be seen from Fig. 3 that the thermomagnetic irreversibility between ZFC and FC curves is present in 0.5 kOe as well as in 5 kOe, for both the bulk and the ball milled samples.

Figure 4 shows the magnetic hysteresis loops for both bulk and ball milled samples measured at 3 K and 10 K after cooling the sample from a temperature well above the transition temperatures. Magnetization does not saturate even in a

FIG. 3. Zero field cooled (ZFC) and field cooled (FC) magnetization vs temperature in 0.5 kOe and 5 kOe for ball milled sample (left panel) and bulk sample (right panel) of Nd_5Ge_3 .

FIG. 4. Magnetic hysteresis loops obtained at 3 K and 10 K for ball-milled as well as bulk Nd_5Ge_3 .

field as high as 90 kOe, in both the cases and in both types of samples. For a given temperature, the bulk sample exhibits higher coercivity (H_C) compared to that of the ball milled sample. We have estimated the coercive field for the bulk to be 20.3 kOe, while that of the ball milled sample is 10.1 kOe at 3 K. At 10 K, the values are 13.4 kOe and 4.8 kOe, respectively. There is a clear field induced irreversible metamagnetic transition in both the samples. The irreversible nature of this transition is retained after ball milling. However, the remanent magnetization value is considerably smaller in the ball milled sample compared to that of the bulk. As can be seen, metamagnetic transition in the virgin curve in the bulk sample is very sharp, it is less sharp in the ball milled sample. The critical field of the metamagnetic transition (at 3 K) for the bulk sample is 22.5 kOe, which decreases to 17.5 kOe after milling. The field induced magnetization jump is already reported in this system.^{14,19} The field induced jump is not only seen in the magnetization isotherm, but in the resistivity and heat capacity isotherms as well.¹⁴ A field induced martensitic strain is assumed to be responsible

for this kind of jumps.^{14,19} One should notice that the virgin curve lies outside the envelope curve in the 3 K hysteresis loops for both the samples. This indicates that the first order nature of the metamagnetic transition earlier observed in the bulk alloy is retained even after ball milling.

The isothermal magnetization curves have been measured in the applied fields up to 70 kOe at various temperatures in the vicinity of the magnetic transition temperature. Figure 5 shows the curves up to 20 kOe for better visibility of the low field part. The temperature was varied from 28 K to 76 K in steps of 3 K for the milled sample whereas the temperature range was 30 K to 69 K for the bulk sample. It is obvious that changes have occurred in the shapes of the magnetic isotherms after milling. In particular, the magnetization increases very rapidly at the start of the field sweep for the milled sample, whereas the trend is different in the bulk case. Nevertheless, the magnetization value for a fixed temperature at the highest applied field (70 kOe) is almost equal for both the samples.

The isothermal magnetization data were further analyzed using the Arrott plot. The idea behind the Arrott plots is that it is possible to expand the magnetic field in terms of the odd powers of magnetization^{20,21}

$$H/M = a_0 + a_1 M^2 + a_2 (M^2)^2 + \dots \quad (1)$$

Arrott plots for the present samples are shown in Fig. 6. The intercepts of the isotherms on the M^2 and H/M axes are the square of the spontaneous magnetization (M_s^2) for $T < T_C$ and the inverse of the zero-field susceptibility (χ_0^{-1}) for $T > T_C$, respectively. Only the high-field linear region was used for the analysis because the plots deviate from linearity at low fields due to demagnetization effect and magnetic domains reorientation.²¹ Thus, we can obtain (M_s^2) and (χ_0^{-1}) by extrapolating the high field portion of the curves. The spontaneous magnetization $M_s(T)$, and inverse initial susceptibility $\chi_0(T)^{-1}$ both follow a power law with a set of interdependent critical exponents β , γ as, $M_s \propto |t|^{-\beta}$ and $\chi_0(t) \propto t^{-\gamma}$, where $t = (T - T_C)/T_C$. We

FIG. 5. Isothermal magnetization curves obtained at different temperatures in ball milled and bulk samples of Nd_5Ge_3 .

FIG. 6. Isothermal H/M vs M^2 plots of ball milled and bulk Nd_5Ge_3 . Lines are the polynomial fits to the high field portion of the curves.

can define $T^* = [d/dT(\ln\chi_0^{-1})]^{-1} = (T - T_C)/\gamma$. Thus, fitting the data of T^* versus T with a straight line gives the value of γ and T_C . The β value can be calculated from the $\ln(M_s)$ versus $\ln(t)$ using same T_C value obtained from T^* versus T . The estimated γ and β values are 1.28 and 0.23 for the bulk sample, where as those values for the milled sample are 0.96 and 0.89. The values in the case of the bulk are quite expected for a three dimensional Heisenberg model. However, the β value for the ball milled sample is exceptionally large.

The magnetic entropy change can be derived by using the Maxwell relation given by,

$$\Delta S_M(T, \Delta H)_{\Delta H} = \int_{H_i}^{H_f} \left(\frac{\partial M(H, T)}{\partial T} \right)_H dH. \quad (2)$$

The magnetic entropy change, ΔS_M , can be calculated from the magnetization isotherm data using the following numerical formula:

$$\Delta S_M(T_i, \Delta H) = \sum_i \frac{(M_{i+1} - M_i)}{(T_{i+1} - T_i)} \Delta H_i, \quad (3)$$

where M_i and M_{i+1} are the magnetization values measured at temperatures T_i and T_{i+1} for a field change ΔH_i . The calculated ΔS_M values for different field changes of the ball milled and bulk samples are shown as a function of temperature in Fig. 7. The maximum ΔS_M values of 5 J/kg K and 4.9 J/kg K are found at 44.5 K and 52.5 K (near their anti-ferromagnetic transitions) for 70 kOe for ball milled and bulk samples, respectively. The corresponding values for 50 kOe are 3.8 J/kg K and 3.4 J/kg K. It is important to note that the sign and the magnitude of the maximum magnetic entropy change remain the same even after milling. However, the operating temperature of the material is reduced by 8 K after ball milling.

Apart from ΔS_M , another important criterion to evaluate the quality of magnetic refrigerant materials is the relative cooling power (RCP). The RCP is estimated as the area enclosed by the ΔS_M versus T curve between the points corresponding to the full width at half maximum, i.e.,

$RCP = \int_{T_1}^{T_2} |\Delta S_M| dT$, where T_1 and T_2 are the temperatures corresponding to both sides of the half maximum value of ΔS_M . The RCP values calculated from the ΔS_M - T plot, respectively yielded approximate values of 136 J kg⁻¹ for the ball milled sample and 147 J kg⁻¹ for the bulk sample, for a field change of 70 kOe. For a field change of 50 kOe, the respective values are 94 J kg⁻¹ and 102 J kg⁻¹. Although the ΔS_M value is moderate, the RCP value is considerably high. This is because of the spread of the ΔS_M peaks over a wide temperature range. The RCP value of the present compound is comparable to many other promising materials such as amorphous $\text{Fe}_{76}\text{Cr}_{8-x}\text{Mo}_x\text{Cu}_1\text{B}_{15}$ ribbons, $(\text{Fe}_{70}\text{Ni}_{30})_{88}\text{Zr}_7\text{B}_4\text{Cu}$ nanocomposite powder, $(\text{FeNi})\text{ZrB}$ Alloy etc.²²⁻²⁴

IV. DISCUSSION

The results presented in the above show that ball milling has affected the magnetic properties of Nd_5Ge_3 to some extent though there is no change in the crystal structure. While the saturation magnetization and the magnetic entropy

FIG. 7. Magnetic entropy change ($-\Delta S_M$) as a function of temperature for both ball-milled and bulk samples of Nd_5Ge_3 .

change are more or less retained as in bulk, the thermo magnetization behavior and the isothermal magnetization trend in the particles are different as compared to the bulk. The fact that the sharpness of the metamagnetic transition is less sharp in the case of the ball milled sample shows that the first order nature of the transition has reduced with reduction in particle size. In fact the low field part of the virgin curve in the ball milled sample shows a negative curvature, while that of the bulk sample shows a positive curvature. The same trend can be seen at higher temperatures as well (Fig. 5). This clearly suggests that there is a net increase in the ferromagnetic component. This is also evident from the M-T plot shown in Fig. 2. These results clearly indicate that the balance between the antiferromagnetic and ferromagnetic exchange couplings that is present in the bulk alloy is broken after size reduction. The large values of coercivity and remanence along with the non saturation tendency of the M-H plots suggest that the magnetic anisotropy of the ball milled powder is quite large.

V. CONCLUSIONS

In conclusion, we have successfully synthesized fine particles of Nd_5Ge_3 compound by the ball milling technique. The coercive field and remnant magnetization decrease considerably after milling. There is an increment of the ferromagnetic component in the fine particles of the bulk antiferromagnetic compound. An analysis based on Arrott plots show that the critical exponents show some difference between the bulk and the ball milled samples. Regarding the magnetocaloric effect, the maximum magnetic entropy change associated with the second order magnetic transition for both bulk and ball milled sample is similar, except that the operating temperature is shifted to lower temperatures after milling.

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