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The effect of distributed exchange parameters on magnetocaloric refrigeration capacity in amorphous and nanocomposite materials

N. J. Jones,^{a)} H. Ucar, J. J. Ipus, M. E. McHenry, and D. E. Laughlin

Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, USA

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The temperature dependent magnetization of nanocomposite alloys has been fit with a modified Handrich-Kobe equation with an asymmetric exchange fluctuation parameter combined with the Arrott-Noakes equation. The two equations of state are combined to calculate the entropy change in the magnetocaloric effect associated with the ferromagnetic to paramagnetic phase transformation. The complete fit for the $M(T)$ of $(\text{Fe}_{70}\text{Ni}_{30})_{88}\text{Zr}_7\text{B}_4\text{Cu}$ nanocomposite powder is accomplished by combining the two theories. We investigate the broadening of the second-order transition arising from asymmetric exchange parameters and resulting from the fluctuations of interatomic spacing found in an amorphous matrix and the asymmetric dependence of exchange energy on interatomic spacing. The magnetic entropy curve revealed extra broadening with a refrigeration capacity (RC) value of 135 J/kg at 5 T, which is comparable to $(\text{Fe}_{76}\text{Cr}_{8-x}\text{Mo}_x\text{Cu}_1\text{B}_{15})$ ribbons, which have a RC value of 180 J/kg for the same applied field. Broadening of the magnetic entropy can lead to larger RC values and a wider working temperature range, making nanocomposite alloys promising for magnetocaloric applications. © 2012 American Institute of Physics. [doi:10.1063/1.3679456]

I. INTRODUCTION

Soft nanocomposite alloys have the potential to be good candidates for magnetocaloric applications. Not only do they possess unique amorphous alloy properties such as having low hysteresis losses, low electrical resistivity, and tuneable Curie temperatures, T_C , with minor compositional changes, they are also easy to suspend in solutions thus providing versatility in applications.

The performance of the alloys is assessed by a parameter called refrigeration capacity. According to Wood and Potter's definition of refrigeration capacity,¹ peak magnitude and width are equally important thus making it a suitable metric for comparing different alloys. The magnetocaloric response of soft amorphous alloys has been fit using the Arrott-Noakes equation by Franco *et al.* around the transition temperature.² However, this equation does not adequately approximate the magnetic response of the alloy at temperatures well below T_C .

Well below T_C , the temperature dependence of magnetization can be approximated using the Handrich-Kobe equation with a modified Brillouin function.³ Additionally, this equation of state helps us understand the extra broadening in ΔS_M resulting from the amorphous phase of the nanocomposites. According to the Bethe-Slater curve,^{4,5} fluctuations in atomic spacing, as well as other disorder at defects and interfaces can lead to an asymmetric dependence of the exchange interactions. These change the magnetization behavior, which ultimately introduces extra broadening in the magnetic entropy response of the alloy. In this paper, we combine the two aforementioned equations of states to have a better description

of $M(T)$ for soft nanocomposite alloys. This will lead to a better description of magnetic entropy change, $\Delta S_M(T)$, and more accurate predictions of refrigeration capacity.

II. EXPERIMENTAL PROCEDURE

Amorphous ribbons of $(\text{Fe}_{70}\text{Ni}_{30})_{88}\text{Zr}_7\text{B}_4\text{Cu}_1$ (typically 2–3 mm wide and $\sim 20 \mu\text{m}$ thick) were obtained by the melt-spinning technique in an Ar atmosphere, starting from arc-melted precursors. The amorphous character of the as-cast alloy was verified by X-ray diffraction (XRD). Ribbons with a length of approximately 30 mm were cut and sealed in hardened steel vials adding hardened steel balls in a ratio of 10:1. This procedure was done under Ar atmosphere in a glovebox. Ball milling of ribbon pieces was performed using a Spex 8000 D mill for 4 h. In order to obtain a single fcc phase, the powdered sample was sealed in a quartz crucible in an Ar atmosphere, annealed in the fcc region of the phase diagram, 700 °C, and quenched in water to stabilize the metastable fcc γ -FeNi phase.

The field dependence of magnetization was measured in a physical properties measurement system (PPMS) with a vibrating sample magnetometer (VSM) head in a liquid helium-cooled Dewar. Magnetization versus temperature was measured with applied fields of 5500 Oe and 500 Oe from 400 K to approximately 100 K, along with hysteresis loops measured every 2 K, with fields up to 90 kOe.

III. FITTING MODELS

Two equations have been studied to describe the magnetization phenomenon of soft magnetic alloys. However, neither one of them was sufficient to approximate the magnetization response at all temperature regimes. Gallagher *et al.*³ modified the Handrich-Kobe equation by introducing

^{a)}Author to whom correspondence should be addressed. Electronic mail: jones.nicholas.j@gmail.com.

two asymmetric exchange fluctuation parameters, δ_+ and δ_- , yielding Eq. (1)

$$\sigma(T) = \frac{1}{2} \{B_s[(1 + \delta_+)x] + B_s[(1 - \delta_-)x]\}. \quad (1)$$

Here, the disorder of the alloy has been taken into consideration by assuming non-symmetric exchange interactions present in the amorphous matrix of the nanocomposite alloy. This equation describes the $M(T)$ response well for low temperatures. However, it is insufficient for the regime where the transition from ferromagnetic to paramagnetic phases occurs.

More recently Franco *et al.*⁶ used the Arrott-Noakes equation (Eq. (2)) to fit their magnetization versus temperature curves around the Curie temperature, and predict the ΔS_M response for soft amorphous alloys.

$$H^{1/\gamma} = a(T - T_C)M^{1/\gamma} + bM^{1/\beta+1/\gamma}. \quad (2)$$

In Eq. (2), β and γ are critical exponents describing the temperature dependence of magnetization and inverse susceptibility, respectively. This equation was accurate in describing and predicting the $M(T)$ near the transition temperature, but it was not as accurate at lower temperatures.

Combining the two equations brings both the low temperature accuracy and disorder within the context of a modified Brillouin function and the Curie tail together into one curve. Because the two equations are implicitly defined or not exactly solvable, the equations need to be evaluated separately and combined using two possible methods. In this work, Mathematica⁷ was used to tabulate data after solving the equations, and then the data was interpolated to create a function that was differentiable.

The Arrott-Noakes equation was both fitted using the hysteresis loops to estimate β and γ , and by adjusting the constants by hand to get a good fit; the fitting procedure as detailed by Franco *et al.*⁶ was not directly applicable to the nanocomposite powders analyzed in this paper, and, as mentioned by Franco *et al.*, a full computer fit of the equation to the curve is unreasonable. Both curves had adjustable parameters for saturation magnetization, Curie temperature, and all other constants. In joining the curves, both matching the slopes and finding the tangent points where the curves overlap was used. The minimum change in slope between the curves or minimum distance between them was calculated in the transition region and used to create a piecewise differentiable function utilizing both equations. Both joining methods provided virtually the same joining temperature. Neither curve had the same trend in slope, however, so the final entropic evaluation, which relies on the derivative of the MvT curve, had a jump in it, due to the inaccuracy. This artifact around 165 K is due to the union of the two theories and is not present in the data. The agreement between the two theories around the transition point is continually being investigated and will be improved with future research.

IV. RESULTS AND DISCUSSION

Figure 1 shows experimental data from the PPMS along with the data fits using both the Arrott-Noakes and

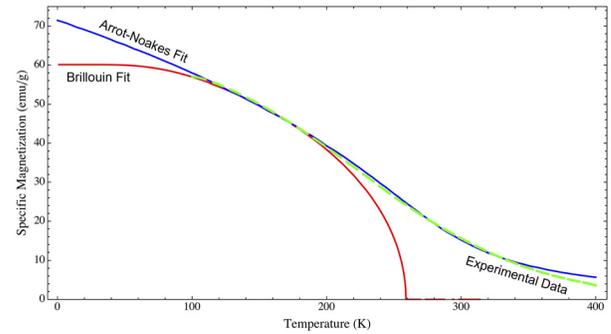


FIG. 1. (Color online) A fit of experimental data (dashed line) using both an exchange-parameter-modified Brillouin equation (lower solid line) and the Arrott-Noakes (upper solid line) equation, with a transition in fitting method around 160 K (data taken with an applied field of 5500 Oe).

modified-Brillouin fit of Gallagher. As can be seen, the Brillouin-fit is necessary at lower temperatures, however, the Curie tail is not accounted for; despite the below-room-temperature Curie temperature, the magnetization still trails off well until around 400 K. This large tail is even true in the lower field data. To fit the data, the Arrott-Noakes fit had the following parameters: $a = 0.79$, $b = 0.00893$, $\beta = 0.428$, $\gamma = 1.38$, $T_C = 216$ K. The Brillouin fit needed modifying parameters as well to fit the curvature of the experimental data: $\delta_+ = 0.75$, $\delta_- = 0.26$, $T_C = 208$ K, $M_s = 60.1$ emu/g. The variable Curie temperature is due to the two different fits and how they understand Curie temperature and is within definitional limits.⁸ The transition region was found to be 163 K for the derivative method, with the proximity method yielding 166 K; the derivative method is used for Fig. 2, below.

The magnetic entropy change due to the application of a magnetic field, H , was evaluated by processing the temperature and field dependent magnetization curves using a numerical approach using Eq. (3):

$$\Delta S_M = \int_0^{H_{\max}} \left(\frac{\partial M}{\partial T} \right)_H dH, \quad (3)$$

where ΔS_M is the magnetic entropy change, M is the magnetization, and T is the temperature. Refrigerant capacity, RC , is calculated using Wood and Potter's method,¹ where $RC = \Delta S_M \Delta T$, and $\Delta T = T_h - T_c$ is the difference between the hot and cold reservoirs. The calculated entropy curve is shown in Fig. 2 for the combined fit and the Arrott-Noakes fit for a maximum field of 5 T. The entropy curve calculated from the actual data is also shown in Fig. 2. The experimental data was smoothed by taking the average of 25 points on each side of a data point (corresponding to an average over ~ 4.5 °C); this smoothing was necessary to reduce the noise present in experimental data as magnified by taking the derivative of the data. The combined fit gives a truer measure of the actual behavior of the material and does not plateau at low temperatures giving a false refrigerant capacity. The discrepancy between the fit and the experimental data is due to the quality of the fit (especially the matching of the experimental slope), as well as the averaging of the data.

By using full width at half maximum (FWHM) as an indication of our RC rectangle, we can calculate the magnetocaloric

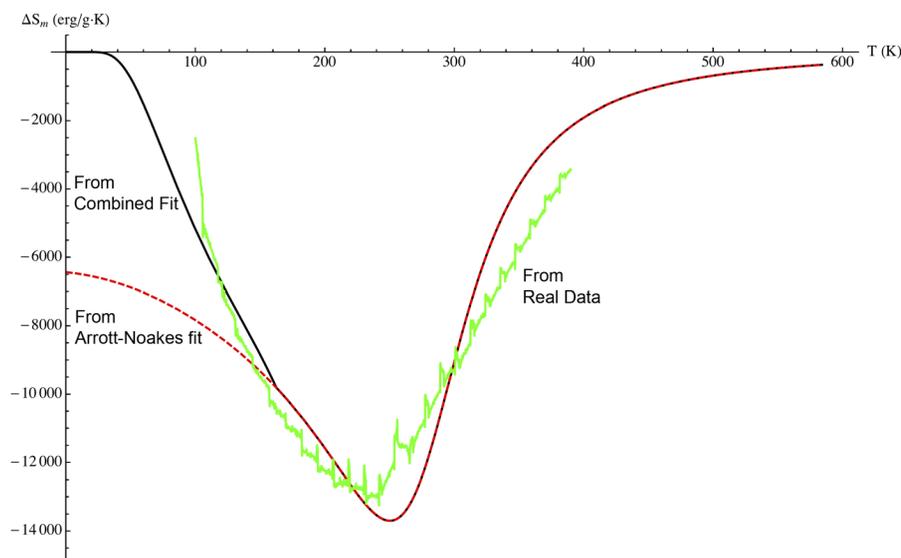


FIG. 2. (Color online) Change in entropy integrated from Fig. 1 with H_{\max} at 5 T using just the Arrott-Noakes equation (dashed), the combined fit (dark line), and averaged experimental data (light gray line).

properties of our powder, as compared with common values from the literature, and comparing the result with the possible value without the combined fit. From Fig. 2, the nanocomposite powder has a refrigerant capacity of 135 J/kg using the full combined fit; when using just the Arrott-Noakes equation, our value would have been much higher and around 186 J/kg. Without the varied exchange parameters, our Brillouin slope would not have been correct and would also have been too steep, reducing the refrigerant capacity from that calculated above.

The RC value for an initial nanocomposite sample shows promise for use in magnetocaloric applications, since it is on par with those found in the literature, specifically when compared with amorphous $(\text{Fe}_{76}\text{Cr}_{8-x}\text{Mo}_x\text{Cu}_1\text{B}_{15})$ ribbons,² which have a RC value of 180 J/kg.

V. CONCLUSIONS

We have shown the efficacy and the necessity of including the full magnetization curve in magnetocaloric calculations of refrigerant capacity. While the Arrott-Noakes equation provides a good fit for the transition temperature, a full fit of the magnetization versus temperature curve is necessary for a truly accurate calculation of RC. When

calculating the values for the nanocomposite powder prepared above, we found that it has strong capabilities as a material for magnetocaloric applications. When considering nanocomposite materials, however, a varied exchange parameter is necessary for the Brillouin fit, as shown by Gallagher and is needed not only to fit the data well but also to get the correct RC value.

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