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A procedure to extract the magnetocaloric parameters of the single phases from experimental data of a multiphase system

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In this work, we propose a method to extract the individual parameters that describe the field dependence of magnetic entropy change of each phase in a multiphase system. This method makes use of the scaling laws of the magnetocaloric effect and can help us to determine the behavior of individual phases and to predict their critical exponents. The accuracy of the procedure is illustrated applying it to ball milled powders, in which an amorphous phase with $T_C$ around room temperature coexists with bcc-Fe type crystallites. The obtained values are in good agreement with those reported in the literature for single phase systems. The proposed method could be applied to other systems where single phase materials cannot be easily obtained in order to characterize the effect of impurities. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4900790]

The magnetocaloric effect (MCE) and the search for magnetic materials with large MCE close to room temperature have received considerable attention in the research community for the prominent application of magnetic refrigeration close to room temperature. In fact, this environment-friendly technology is called to substitute the current gas technology.

In order to compare data obtained from different laboratories, it has to be taken into account that they can be obtained under different experimental conditions, particularly using different maximum magnetic field changes. The understanding of the field dependence of MCE has helped to get a general picture of the different magnetocaloric materials. Moreover, the exponents defining this field dependence are related to the critical exponents of the transition, and there are several studies from different groups, who have found a good agreement between the critical exponents extracted from conventional techniques (e.g., Kouvel-Fisher method) and the results obtained from MCE, e.g., for amorphous and nanocrystalline alloys, manganites, perovskites, and Er$_2$Fe$_7$ system.

Most of these studies are devoted to single phase materials, although pure phases are not always easy to be obtained. Therefore, the study of the field dependence of the magnetic entropy change ($\Delta S_M$) of multiphase materials is an important task. A common way to obtain $\Delta S_M$ is applying the Maxwell relation using the field dependence of magnetization curves as a function of temperature

$$\Delta S_M = \mu_0 \int \left. \frac{\partial M}{\partial T} \right|_H dH,$$

where $M$ is the magnetization, $H$ is the magnetic field, and $T$ is the temperature.

Several works have described the field dependence of $\Delta S_M$ following a power law, $\Delta S_M = aH^n$, where $a$ is a temperature dependent prefactor. Under this approach, there are two temperature ranges where exponent $n$ presents field independent values.

For temperatures well below the Curie temperature, $T_C$, and not high enough applied magnetic fields, the magnetization follows a power law, $\Delta S_M = aH^n$, has been predicted, where $\beta$ and $\gamma$ are the critical exponents of the transition. Values of $n$ between 0.70 and 0.74 have been obtained for different amorphous and nanocrystalline alloys, perovskites, and Er$_2$Fe$_7$ system.

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$$\Delta S_M = \mu_0 \int \left. \frac{\partial M}{\partial T} \right|_H dH,$$

where $M$ is the magnetization, $H$ is the magnetic field, and $T$ is the temperature.

$$H = H_{\text{appl}} - NDM,$$

$\Delta S_M$ is the magnetization, $H$ is the magnetic field, and $T$ is the temperature.
where $H_{\text{app}}$ is the applied magnetic field and $H$ is the internal field.

Otherwise, the knowledge of the critical behavior and the field dependence of the MCE of a particular system could lead to determine its demagnetizing factor. Besides these experimental aspects, in the case of multiphase materials with different Curie temperatures for each phase, it has been shown that, first, the exponent $n$ is field dependent and, second, it presents higher values than those showed for a single phase material at $T_C$.  

In this sense, ball milling leads to microstructures that easily depart from a single phase material due to the presence of impurities or remaining untransformed phases. However, the versatility of this technique and its ability to produce metastable phases make it to be widely used to produce MCE materials. Therefore, a systematic study of the dependence of $n$ on the fraction of typical impurities found in mechanically amorphized samples, may lead to general conclusions that can be easily extended to other systems or production techniques, for which impurity phases are difficult to avoid.

We have studied in previous works the enhancement of MCE in composites (in which components have close Curie temperatures) with respect to single phase systems. In this work, we also explore multiphase systems with the aim of extracting the MCE parameters of a theoretically single phase system from the study of the field dependence of MCE in multiphase systems. In our case, the studied systems are partially amorphous Fe$_{75}$Nb$_{10}$B$_{15}$ alloys prepared via mechanical alloying. Details about sample preparation can be found elsewhere. 

Microstructure shows that, as milling time increases, the fraction of developed amorphous phase increases. Moreover, it was also observed that the amount of dissolved boron into the amorphous matrix increases with milling time. Isothermal magnetization data (using a LakeShore 7407 vibrating sample magnetometer) were corrected taking into account the demagnetizing factor ($N_D = 1/3$), which corresponds to loosely packed spherical powders, as observed by scanning electron microscopy. Finally, these new curves are later used to calculate the magnetic entropy change employing Eq. (1). From the analysis of the field dependence of the magnetic entropy change presented in this study, we are able to obtain the parameters that describe the field dependence of an amorphous phase at its $T_C$ under the approximation of non-interacting phases.

Microstructural evolution with milling time for all studied samples can be found elsewhere. Milled samples show a multiphase character composed by bcc-Fe type crystals and boron inclusions embedded in an amorphous matrix. The diamagnetic character of the boron inclusions makes them irrelevant for the present study.

Figure 1(a) shows the spontaneous specific magnetization, $\sigma_0$, as a function of temperature. The multiphase character of the studied samples is also observed from this measurement, as $\sigma_0$ does not fall completely to zero above the magnetic transition temperature due to the presence of the remaining crystalline phase with a higher Curie temperature. The Curie temperature of the amorphous phase, $T_{\text{C,am}}$, was determined as the inflexion point in $\sigma_0(T)$ curves (Fig. 1(a)). Figure 1(b) shows $T_{\text{C,am}}$ as a function of the crystalline fraction, $X_C$. It can be seen that, as crystalline fraction decreases, $T_{\text{C,am}}$ increases, which was ascribed to higher boron content in the amorphous matrix. In fact, we have previously shown that boron is progressively integrated into the amorphous phase as milling time increases. Moreover, in Fe-based amorphous alloys, the increase in B content up to $\sim 30$ at. % of this element leads to an increase of the Curie temperature.

Figure 2(a) shows the magnetic entropy change for a maximum field change of 1 T as a function of temperature, for different crystalline fractions. It is observed that as crystalline fraction decreases, $|\Delta S_M|$ increases because the main contribution in this temperature range comes from the amorphous phase. The peak temperature also increases, in agreement with the evolution of $T_{\text{C,am}}$.

The temperature dependence of the exponent $n$ is shown in Figure 2(b) for several samples with different crystalline fraction. For $T \ll T_{\text{C,am}}$, the value of $n = 1$ agrees with the expected one for materials presenting ferromagnetic behavior well below its $T_C$. For temperatures above $T_{\text{C,am}}$, an increase of $n$ is observed for all curves, although the expected value for materials showing paramagnetic behavior ($n = 2$) is not reached. These values for exponent $n$ are a consequence of the biphasic character of the samples, and $n$ tends to a value between one (corresponding to ferromagnetic bcc-Fe type impurities) and two (paramagnetic amorphous phase) depending on the crystalline fraction of the sample.
At the transition temperature, $n$ values are field dependent and higher than those observed for single phase amorphous alloys. As in the present case all the studied samples present two magnetic phases, the total magnetic entropy change can be expressed as the sum of the entropy changes due to both the crystalline phase and the amorphous phase, assuming non-interacting phases

$$\Delta S_M = aH^n = a_C X_M H^{n_C} + a_A (1 - X_M) H^{n_A},$$

where the magnetic phase fraction, $X_M = f X_C$, is related by a factor $f$ to the crystalline fraction obtained from X-ray diffraction. It must be taken into account that while $X_C$ represents the amount of material in a crystalline array, the magnetic fraction corresponds to the amount of magnetic atoms into the crystalline phase. The prefactors $a_C$ and $a_A$ correspond to the magnetic entropy change at 1 T of the crystalline and amorphous phase, respectively, being temperature dependent. For the crystalline bcc-Fe type phase, the studied temperature range (around room temperature) is well below its Curie temperature, and a constant value of $a_C$ is a reasonable assumption because this corresponds to the low temperature tails of its expected MCE curve. For the case of the amorphous phase, changes in its $T_C$ with $X_C$, due to the dissolution of boron in the amorphous matrix were observed. Recently, it has been shown that changes in the Fe/B ratio does not significantly affect the peak value of the entropy change for similar Fe-B based amorphous alloys, although $T_C$ is seriously affected. Therefore, the prefactor $a_A$ can be considered independent of $X_C$ at the peak temperature of each sample.

The experimental value of $n$ at the peak temperature of $\Delta S_M$ is related with those of each phase through the following expression:

$$n_p^k = \frac{d \ln(\Delta S_M^p)}{d \ln(H)} = \frac{(X_M a_C n_C H^{n_C} - a_A n_A H^{n_A}) X_M + a_A n_A H^{n_A}}{X_M a_C H^{n_C} + (1 - X_M) a_A H^{n_A}}.\quad(4)$$

Regrouping the terms,

$$\Delta S_M^p n_p^k = (a_C n_C H^{n_C} - a_A n_A H^{n_A}) X_M + a_A n_A H^{n_A}.\quad(5)$$

Equation (5) predicts that $\Delta S_M^p n_p^k$ vs $X_C$, for a constant $H$, should lead to a straight line where both the slope ($m$) and the intercept ($b$) depend on the field $H$ and are defined as

$$m(H) = (a_C n_C H^{n_C} - a_A n_A H^{n_A}) f,$$

$$b(H) = a_A n_A H^{n_A}.\quad(7)$$

Figure 3 shows the values of $n_p^k$, $\Delta S_M^p$, and of the product $\Delta S_M^p n_p^k$ at 1 T as a function of the crystalline fraction determined by XRD. Taking logarithm to both sides of Eq. (7), the values of exponent $n_A$ and prefactor $a_A$, corresponding to the amorphous phase, could be obtained from a linear fitting of $\ln(b)$ vs $\ln(H)$ data (Fig. 4(a)), being $n_A = 0.757 \pm 0.012$ and $a_A = 0.596 \pm 0.011$ J kg$^{-1}$ K$^{-1}$ T$^{-0.757}$. The estimated exponent for a pure amorphous phase agrees well with typical ones.
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Experimental work of this model, we have studied the field dependence of the specific magnetization of the bcc-Fe type phase (135 emu/g) of the crystalline bcc-Fe(Nb,B) type phase, with Curie temperature close to room temperature, and remaining bcc-Fe type crystallites. The value of the experimentally obtained exponent \( n \) of the composite decreases as \( X_C \) decreases. The present analysis allows us to obtain the parameters that describe the field dependence for the amorphous phase at its \( T_C \). The obtained results

\[
\eta_A = 0.757 \pm 0.012 \quad \text{and} \quad a_C = 0.596 \pm 0.011 \quad \text{J kg}^{-1} \text{K}^{-1} \quad T^{-0.757}
\]

are in good agreement with those observed for pure amorphous materials obtained by rapid quenching. In the case of \( \eta_A \), its value can be related with the critical exponents of the transition. The described method can be easily extended to analyze other systems for which pure phase materials are difficult to obtain.

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FIG. 4. Linear fitting of (a) \( \ln(a_C H^m) \) as a function of \( \ln(H) \) and (b) \( aCf - aCH^m \) as a function of \( H^{-0.234} \). Lines correspond to the linear fit to the data.

\[
m(H) = \frac{m(C)}{H} = f a_C - f n_a a_H^{-n_a-1},
\]

where a linear fitting of \( m(H) \) vs \( H^{m-1} \) (Fig. 4(b)) provides the values of \( a_c = 0.118 \pm 0.007 \quad \text{J kg}^{-1} \text{K}^{-1} \quad \text{T}^{-1} \) and \( f = 1.74 \pm 0.11 \). The low value of \( a_c \) is justified by the very high value of the Curie temperature of the crystalline phase. Moreover, the value of \( f \) can be understood due to the higher specific magnetization of the bcc-Fe type phase (135 emu/g) with respect to that of the amorphous phase (90 emu/g), as was showed in a previous work.

In conclusion, we have developed a model based on noninteracting phases and assuming that the magnetic entropy change of a multiphase material can be expressed as the sum of the individual contributions of each phase. In the framework of this model, we have studied the field dependence of the entropy change of a composite formed by an amorphous phase, with Curie temperature close to room temperature, and remaining bcc-Fe type crystallites. The value of the...