AIP Journal of Applied Physics

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Citation: Journal of Applied Physics **117**, 17A710 (2015); doi: 10.1063/1.4907188
View online: http://dx.doi.org/10.1063/1.4907188
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/117/17?ver=pdfcov
Published by the AIP Publishing

JOURNAL OF APPLIED PHYSICS **117**, 17A710 (2015)

High-magnetic field characterization of magnetocaloric effect in FeZrB(Cu) amorphous ribbons

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(Presented 6 November 2014; received 22 September 2014; accepted 16 October 2014; published online 6 February 2015)

The magnetic and magnetocaloric properties of a series of Fe-rich FeZrB(Cu) amorphous ribbons were investigated under magnetic field values up to μ_0H of 8 T. A correlation between the saturation magnetization and the maximum magnetic entropy change $|\Delta S_M{}^{peak}|$ is clearly evidenced. Although these metallic glasses show relatively low $|\Delta S_M{}^{peak}|$ values (from 3.6 to 4.4 J kg^{-1} K^{-1} for $\mu_0\Delta H = 8$ T), the $\Delta S_M(T)$ curve broadens upon the increase in $\mu_0\Delta H$, giving rise to a large refrigerant capacity *RC* (above 900 J kg^{-1} for $\mu_0\Delta H = 8$ T). Using the universal curve method for rescaling the $\Delta S_M(T,\mu_0\Delta H)$ curves, we found a collapse of the curves around the Curie temperature. However, in the low-temperature range the curves do not match into a single one due to the existence of magnetic frustration. © *2015 AIP Publishing LLC*.
[http://dx.doi.org/10.1063/1.4907188]

INTRODUCTION

Fe-rich FeZrB(Cu) metallic glasses display striking magnetic behaviors such as low-temperature magnetic frustration and magneto-volume anomalies below the Curie temperature, T_C, due to the strong competition between Fe-Fe magnetic interactions.[1–4] Furthermore, the value of T_C scales almost linearly with the Fe content in the 210–350 K range,[4,5] and can be easily selected by changing the composition. The latter is of particular interest in magnetocaloric (MC) materials for: (a) developing active magnetic regenerators operating around room temperature[6] and (b) designing two-phase MC composites with a table-like shape of the $\Delta S_M(T)$ curve. This usually improves the refrigerant capacity, *RC*,[7,8] an important figure of merit that measures the transferable heat in an ideal thermodynamic cycle from the cold to the hot reservoirs at temperatures T_{cold} and T_{hot}, respectively.[9,10]

However, for these purposes, the materials must fulfill other requirements: to exhibit analogous values for the maximum magnetic entropy change, $|\Delta S_M{}^{peak}|$, and also similar shaped $\Delta S_M(T)$ curves. Previous studies reported that for $\mu_0\Delta H \leq 5$ T, the FeZrBCu ribbons satisfy both conditions.[11] Moreover, the similarity of their $\Delta S_M(T)$ curves was verified in the framework of the so-called "universal curve."[11] In this way, it was shown theoretically, and verified phenomenologically for $\mu_0\Delta H$ up to 5 T, that the $\Delta S_M(T,\mu_0\Delta H)$ curves of different materials with similar critical exponents collapse into a single curve when properly rescaled.[12–14] The so-called "universal curve" serves to extrapolate the magnetic entropy change to higher $\mu_0\Delta H$ values and wider temperature ranges,[15] and to reveal the presence of magnetic inhomogeneities.[11]

In this study, we investigate the magnetic and magnetocaloric properties of several Fe-rich FeZrB(Cu) amorphous ribbons and test the validity of the phenomenological universal curve up to high values of the magnetic field change $\mu_0\Delta H$ of 8 T.

EXPERIMENTAL PROCEDURE

Seven amorphous ribbons with chemical composition given by: $Fe_{90}Zr_{10}$, $Fe_{90}Zr_9B_1$, $Fe_{91}Zr_7B_2$, $Fe_{90}Zr_8B_2$, $Fe_{88}Zr_8B_4$, $Fe_{86}Zr_7B_6Cu_1$, and $Fe_{87}Zr_6B_6Cu_1$ were fabricated by melt spinning from arc melted bulk alloys. The amorphous character of the samples was confirmed by X-ray diffraction (no traces of crystalline phases were detected).

Magnetization measurements were performed on a Quantum Design PPMS-9T platform by using the vibrating sample magnetometer option. The T_C of samples was determined from the temperature dependence of the magnetization, $M(T)$, measured under a low applied magnetic field μ_0H of 5 mT. The isothermal magnetization curves, $M(\mu_0H)$, were measured up to $\mu_0H = 8$ T from 50 to 400 K with *T*-steps of 10 K. The $\Delta S_M(T)$ curve for each sample was obtained by numerical integration of the Maxwell relation (i.e., $\Delta S_M(T,\mu_0H) = \mu_0\int_0^{\mu_0H}\left(\frac{\partial M(T',\mu_0H')}{\partial T'}\right)_{T'=T}dH'$).[6]

For a given value of the magnetic field change $\mu_0\Delta H$, *RC* can be estimated on a first approach as the product $|\Delta S_M{}^{peak}| \times \delta T_{FWHM}$.[10] In this definition, δT_{FWHM}

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corresponds to the full-width at half-maximum of the $\Delta S_M(T)$ curve [i.e., $\delta T_{FWHM}(\mu_0\Delta H) = T_{hot} - T_{cold}$, with T_{hot} and T_{cold} the working temperature ends of the refrigerant thermodynamic cycle].

The phenomenological universal curve was obtained by an appropriate renormalization of the $\Delta S_M(T)$ curves determined for the various $\mu_0\Delta H$ values. The procedure for each $\mu_0\Delta H$ value is:[16] (a) the $\Delta S_M(T)$ curves are normalized to $|\Delta S_M^{peak}|$; (b) the temperature axis is rescaled below and above T_C by imposing two temperatures, Tr_1 and Tr_2, related to two reference points at each side of the $\Delta S_M(T)$ curve that corresponds to a certain fraction of $|\Delta S_M^{peak}|$ (i.e., $a \times |\Delta S_M^{peak}|$, with a an arbitrary value between 0 and 1)

$$\begin{aligned} \theta &= -(T - T_C)/(Tr_1 - T_C) \quad T < T_C, \\ \theta &= (T - T_C)/(Tr_2 - T_C) \quad T > T_C. \end{aligned} \tag{1}$$

It must be pointed out that these reference temperatures do not have a physical meaning due to the arbitrariness of a. However, a is generally chosen equal to 0.5 since it corresponds to the half maximum and, therefore, Tr_1 and Tr_2 correspond to T_{cold} and T_{hot}, respectively.

RESULTS AND DISCUSSION

Fig. 1(a) shows the typical low-field $M(T)$ curves measured on heating after a zero-field-cooling procedure. All the samples exhibit a broad second-order magnetic phase transition. The value of T_C was estimated from the minimum of the $dM/dT(T)$ curve. As listed in Table I, T_C values range between 210 and 320 K. Fig. 1(c) depicts the curves at 50 K normalized to their respective value at $\mu_0 H = 8$ T. The magnetic anisotropy increases with the Fe-content; in fact, for Fe at. % > 88, the ribbons hardly reach the saturation state at 8 T. Such behavior arises from the magneto-volume instabilities of these metallic glasses.[1,2] We have estimated the saturation magnetization, M_S, of the ribbons by fitting the corresponding isothermal $M(\mu_0 H)$ curve [a typical set of these $M(\mu_0 H)$ curves is given in Fig. 1(b) for $Fe_{91}Zr_7B_2$] using an approach-to-saturation law.[17] The temperature dependence of M_S (see inset in Fig. 1) shows that the higher the Fe content, the more pronounced the decrease of the $M_S(T)$ curves and the lower the saturation magnetization.

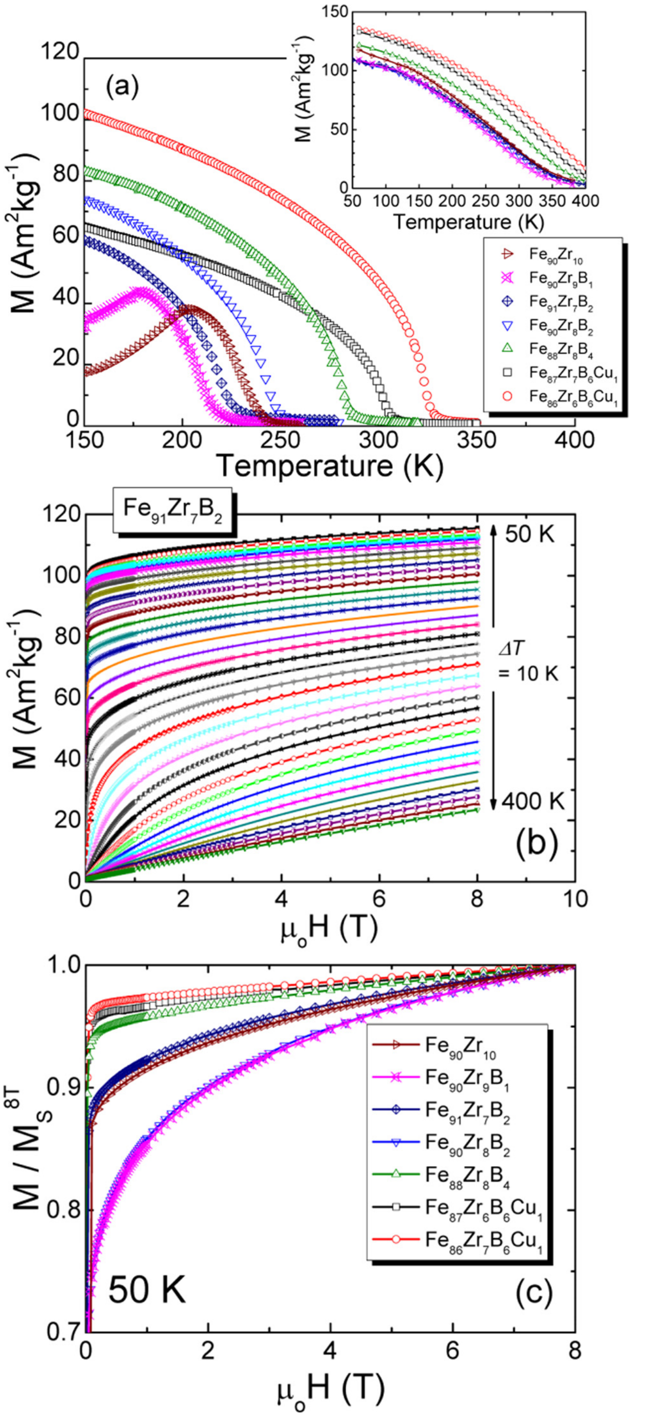

FIG. 1. $M(T)$ curves measured under $\mu_0 H = 5$ mT (a), and $M_S(T)$ curves obtained from the fitting of the $M(\mu_0 H)$ curves to the approach-to-saturation law (inset). (b) Set of $M(\mu_0 H)$ measured from 50 to 400 K for the $Fe_{91}Zr_7B_2$ alloy. (c) $M(\mu_0 H)$ curves at 50 K normalized to the value at $\mu_0 H = 8$ T.

The samples exhibit broad $|\Delta S_M(T)|$ curves [see Fig. 2(a)] and moderate peak values for the magnetic entropy change, $|\Delta S_M^{peak}|$, in consonance with the wide magnetic phase transition observed in the $M(T)$ curves [see Fig. 1(a)]. It is also worth noting that the temperature corresponding to $|\Delta S_M^{peak}|$, T^{peak}, as well as the value of $|\Delta S_M^{peak}|$ follows a linear dependence with the at. % of Fe [see Fig. 2(b)], likewise T_C (see Table I & Refs. 4 and 5). In Fig. 2(c), we show the $|\Delta S_M^{peak}|$ vs. the saturation magnetization estimated at 50 K ($M_{S,50}$) for $\mu_0\Delta H = 2$, 5, and 8 T. A linear correlation between both magnitudes (with a positive slope increasing from 0.012 up to 0.024 when $\mu_0\Delta H$ increases from 2 to 8 T) is clearly evidenced. The highest $|\Delta S_M^{peak}|$ value corresponds to the alloy with the largest $M_{S,50}$ value (i.e., $M_{S,50} = 136$ A m^2 kg^{-1} for $Fe_{86}Zr_7B_6Cu_1$). A similar $|\Delta S_M^{peak}|$ vs. M_S relationship has been observed in other amorphous systems.[18,19] Owing to their inferior M_S values and a broader ferro-to-paramagnetic phase transition, these FeZrB(Cu) amorphous alloys exhibit a lower $|\Delta S_M^{peak}|$ than that of pure Gd.[20] However, as shown in the inset of Fig. 3, the δT_{FWHM} values of these alloys for $\mu_0\Delta H = 5$ T exceed 180 K [and continuously rises as $\mu_0\Delta H$ does, because T_{cold} and T_{hot} go to lower and higher values, respectively], i.e., more than twice the working temperature span reported for Gd ($\delta T_{FWHM} \sim 70$ K at 5 T).[20] These huge width of the $|\Delta S_M(T)|$ curves explain why the *RC* values

TABLE I. $|\Delta S_M^{peak}|$, δT_{FWHM}, and RC for $\mu_0\Delta H = 2$, 5, and 8 T for the studied amorphous alloys.

		$\|\Delta S_M^{peak}\|$ (J kg^{-1} K^{-1})			δT_{FWHM} (K)			RC (J kg^{-1})		
Sample	T_C (K)	2 T	5 T	8 T	2 T	5 T	8 T	2 T	5 T	8 T
$Fe_{90}Zr_{10}$	230 (5)	1.3	2.7	3.9	154	196	229	194	497	801
$Fe_{90}Zr_9B_1$	210 (5)	1.3	2.7	3.8	153	190	215	198	492	795
$Fe_{91}Zr_7B_2$	215 (5)	1.2	2.5	3.6	150	190	216	177	462	755
$Fe_{90}Zr_8B_2$	240 (5)	1.3	2.6	3.7	158	201	225	198	514	830
$Fe_{88}Zr_8B_4$	280 (5)	1.3	2.8	4.0	154	198	226	201	551	905
$Fe_{87}Zr_6B_6Cu_1$	300 (5)	1.6	3.0	4.3	143	197	226	208	590	953
$Fe_{86}Zr_7B_6Cu_1$	320 (5)	1.6	3.1	4.4	139	193	…	205	582	…

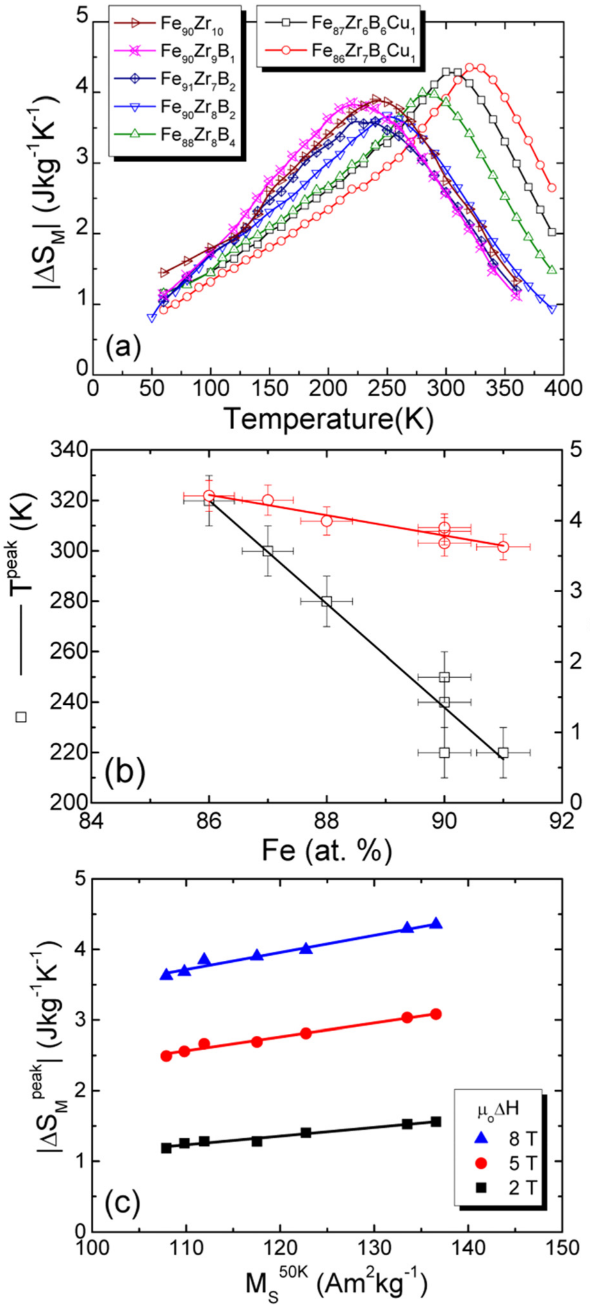

FIG. 2. (a) $\Delta S_M(T)$ curves for a magnetic field change $\mu_0\Delta H$ of 8 T. (b) $|\Delta S_M^{peak}|$ and T^{peak} as a function of the Fe at. % for an applied magnetic field change $\mu_0\Delta H = 8$ T. (c) $|\Delta S_M^{peak}|$ *vs.* M_S at 50 K for $\mu_0\Delta H = 2$, 5, and 8 T. Lines are guides for the eyes.

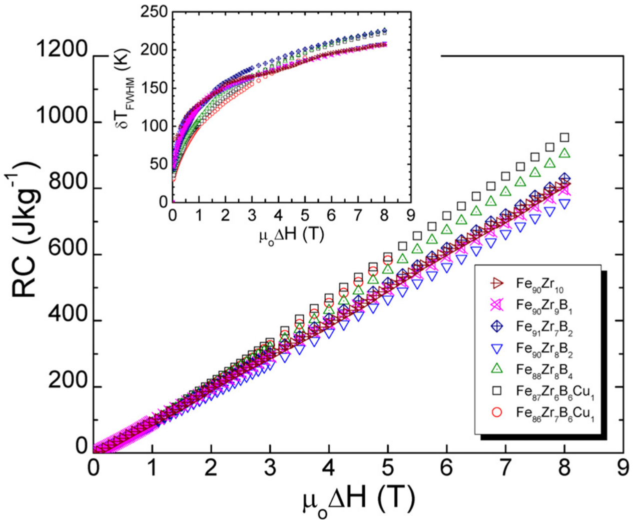

FIG. 3. Applied magnetic field change dependence of the refrigerant capacity, RC. Inset: δT_{FWHM} as a function of $\mu_0\Delta H$.

reach ca. 90% that for pure Gd (Ref. 20) [see Fig. 3 and Table I for the RC values under a magnetic field change of 2, 5, and 8 T].

The degree of asymmetry exhibited by the $|\Delta S_M(T)|$ curves [see Fig. 2(a)] can be measured through the applied magnetic field dependence of $(T_{hot} - T^{peak}) - (T^{peak} - T_{cold})$ [see inset in Fig. 4(b)]. In the case of positive values, $|\Delta S_M|$ decreases slowly for $T > T_C$, whereas the negative values indicate a less marked variation of $|\Delta S_M|$ in the magnetically ordered state ($T < T_C$). The asymmetry is positive for all the studied samples under low magnetic field changes and reaches a maximum for a value of $\mu_0\Delta H$ that depends on the alloy composition. However, only the alloys with 86 and 87 Fe at. % keep the positive values in the whole magnetic field range. As expected, the effect of these asymmetries also appears in the universal curve. Fig. 4(a) shows the rescaled $\Delta S_M/\Delta S_M(\theta)$ curves for the $Fe_{86}Zr_7B_6Cu_1$ amorphous alloy. In the magnetically ordered state, the $\Delta S_M/\Delta S_M(\theta)$ curves for different values of the magnetic field change do not overlap for $\theta < -1$; this behavior is present in all the studied ribbons, even for low values of the magnetic field change. These irregularities indicate the existence of magnetic anomalies at low temperatures,[9] due to either magnetic frustration or strong magneto-volume coupling. However, the curves match for $\theta > -1$, where magnetic frustration is no longer expected, thus validating the existence of a phenomenological universal curve. Moreover, all the rescaled $\Delta S_M/\Delta S_M(\theta)$ curves for $\mu_0\Delta H = 8$ T collapse in the normalized temperature range corresponding to the full width at half maximum (T_{cold} corresponds with $\theta = -1$ and T_{hot} with $\theta = 1$) and for higher temperatures, [see Fig. 4(b)], thus indicating a similar mechanism of the ferro-to-paramagnetic transition for the studied ribbons.

SUMMARY AND CONCLUSIONS

We have studied the magnetic and MC properties of a set of FeZrB(Cu) amorphous alloys under applied magnetic field values up to $\mu_0H = 8$ T. The saturation magnetization

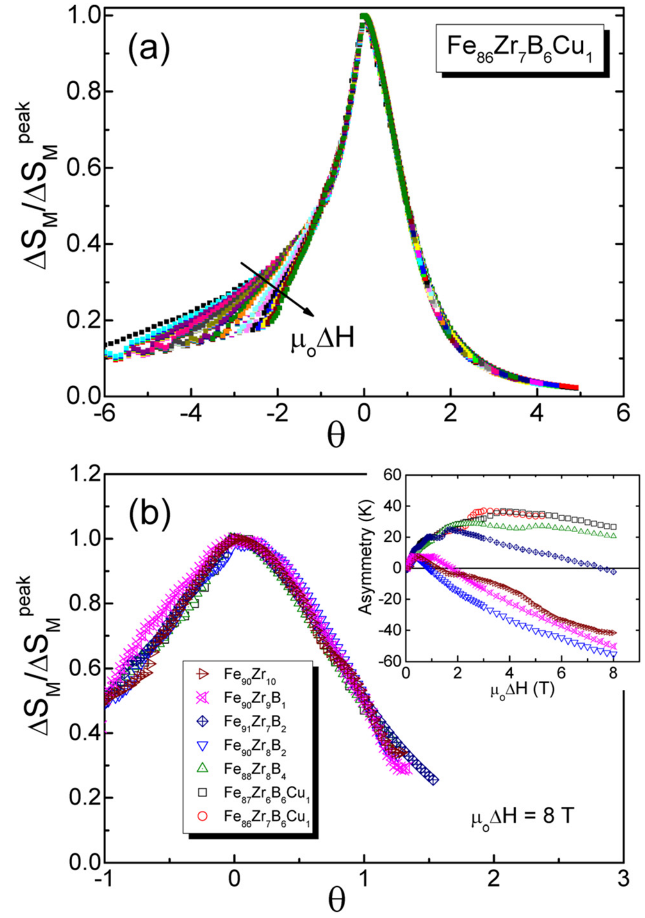

FIG. 4. (a) Rescaled $\Delta S_M(\theta)$ curve of the $Fe_{86}Zr_7B_6Cu_1$ ribbon (see text for details). (b) Comparison of the FeZrBCu alloys universal curves for $\mu_0\Delta H = 8$ T in a rescaled temperature range. Inset: Magnetic field dependence of the asymmetry of the $\Delta S_M(T)$ curves, defined as the difference $(T_{hot} - T^{peak}) - (T^{peak} - T_{cold})$.

and the temperature of the maximum of the magnetic entropy change decrease linearly with the increase of Fe-content. Although the maximum values for the magnetic entropy change are rather low (between 3.6 and 4.4 J kg^{-1} K^{-1} for $\mu_0\Delta H = 8$ T), the broad $|\Delta S_M(T)|$ curves give rise to large $RC(\mu_0\Delta H)$ values (ca. 90% of pure gadolinium at $\mu_0\Delta H = 5$ T). We also tested the validity of the phenomenological universal curve under high-applied magnetic field values: when using two reference points, the curves overlap at rescaled temperatures $\theta > -1$, but the existence of magnetic frustration avoids the collapse in the low temperature range. Nevertheless, the universal curves of all the samples overlap for $\theta > -1$, thus suggesting a similar magnetic behavior in the ferro-to-paramagnetic transition for these Fe-rich FeZr-based amorphous ribbons.

ACKNOWLEDGMENTS

This work has been financially supported by: (a) projects CB-2010-01-156932 (CONACyT, Mexico), MAT2011-27573-C04 (MINECO, Spain), and IT711-13 (Basque Government, Spain); (b) Laboratorio Nacional de Investigaciones en Nanociencias y Nanotecnología (LINAN, IPICYT). C. F. Sánchez-Valdés thanks LINAN, IPICyT, and CONACyT (Project No. CB-2012-01-183770) for supporting his postdoctoral stay.

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