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Identifying the Critical Point of the Weakly First Order Itinerant Magnet $DyCo_2$ with Complementary Magnetization and Calorimetric Measurements.

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We examine the character of the itinerant magnetic transition of $DyCo_2$ by different calorimetric methods, thereby separating the heat capacity and latent heat contributions to the entropy - allowing direct comparison to other itinerant electron metamagnetic systems. The heat capacity exhibits a large lambda-like peak at the ferrimagnetic ordering phase transition, a signature that is remarkably similar to $La(Fe,Si)_{13}$ where it is attributed to giant spin fluctuations. Using calorimetric measurements we also determine the point at which the phase transition ceases to be first order: the critical field, $\mu_0 H_{crit}$ = 0.4±0.1 T and T_{crit} = 138.5±0.5 K, and we compare these to values obtained from analysis of magnetization by application of the Shimizu inequality for itinerant electron metamagnetism. Good agreement is found between these independent measurements, thus establishing the phase diagram and critical point with some confidence. In addition we find that the often-used Banerjee criterion may not be suitable for determination of first order behavior in itinerant magnet systems.

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75.30.Kz: Magnetic phase boundaries (including magnetic transitions, metamagnetism, etc.)

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I. INTRODUCTION

With recent interest in first order magnetic phase transitions for room temperature refrigeration,[1,2,3] certain classes of materials have generated much attention. In particular, the cubic $NaZn_{13}$-type $La(Fe,Si)_{13}$[4] and the hexagonal Fe_2P-type $Mn_xFe_{1.95-x}P_{1-y}Si_y$[5] - both of which are itinerant electron metamagnets (IEM) - show significant promise. $La(Fe,Si)_{13}$ has a giant entropy change with large associated latent heat and a signature giant lambda-like heat capacity at the transition,[6,7,8] whereas $Mn_xFe_{1.95-x}P_{1-y}Si_y$ has been much less studied. The study of these systems reinvigorates an interest in IEM systems and in particular the nature of the transition and how it evolves in applied magnetic field - all -important for magnetocaloric applications.

RCo_2 (where R is the rare earth element) is a well established IEM system.[9] The choice of R affects the lattice parameter, and as a result the bulk magnetic behavior via 4f-3d exchange.[10] Furthermore, the lattice parameter, a, can be tuned such that a small change in applied field, temperature, and/or pressure can induce magnetic order (7.05 Å < a < 7.22 Å),[6,11] and an associated volume change (or distortion) occurs to reduce the increase in energy due to overlap of 3d bands. If that volume change is sufficiently large, the phase transition will be first order[12] and itinerant electron metamagnetism occurs.[13]

In $DyCo_2$ - an IEM of potential interest for low temperature magnetocaloric applications[14] - a first order phase transition was predicted[13,15] and observed by XRD in zero field, where a cubic-tetragonal distortion occurs alongside the magnetic transition[16,17] (these same XRD measurements showed that in a magnetic field of 4 T the phase transition is continuous). Nevertheless, in spite of the extensive work on this system, the details of the *H-T* phase diagram are much less established, and the critical point (where the first order transition disappears) has not previously been determined.[18,19,20]

Here we study $DyCo_2$ using both magnetic and calorimetric methods – to investigate whether there is a giant enhancement of the heat capacity, C_p, close to T_c as previously observed in the $La(Fe,Si)_{13}$ system.[6,7] We obtain the latent heat and C_p separately, so that we can also establish

the relationship between latent heat and hysteresis in this system. We find that both vanish at a critical point which we establish in the *H-T* phase diagram. We also employ the Shimizu inequality (derived from spin fluctuation theory)[21,22] that defines the onset of IEM to determine the field, H_{crit}, and temperature, T_{crit}, of the critical point. Finally, we discuss the validity of the Shimizu inequality compared to the widely used Banerjee criterion[23] for determination of the onset of first order behavior.

One technical complication is that often it is difficult experimentally to distinguish a latent heat from a rapidly-varying heat capacity, as will be discussed in detail below. For consistency in nomenclature, we refer to the true heat capacity always as "C_p", and in any measurement that may include a latent heat contribution as "total heat capacity".

II. EXPERIMENTAL DETAILS

The $DyCo_2$ alloy was prepared by arc melting the pure metals under purified argon atmosphere. Dysprosium was obtained from the Materials Preparation Center[24] of Ames Laboratory of U.S. Department of Energy, and major impurities (in atomic ppm) were: O – 1190 and C – 459. Cobalt was purchased from Johnson Matthey Chemicals Limited (Alfa Aesar) and was 99.95 at. % pure. A small amount (2 at. %) of Dy has been added in excess to the stoichiometrically calculated Dy:Co ratio in order to a) compensate for the weight loss of Dy during arc-melting; and b) prevent the formation of the congruently-melting $DyCo_3$ phase (a common impurity in $DyCo_2$, which forms from $DyCo_3$ and liquid by a peritectic reaction). An ~8 g button was re-melted 3 times and then broken into a few pieces. The heat treatment was performed in a sealed quartz ampoule filled with inert gas at 1173 K for 5 days. Phase purity of the material was checked by X-ray powder diffraction analyses followed by Rietveld refinement of the X-ray diffraction patterns. X-ray analyses of the heat-treated sample revealed no detectible impurities (within the 2 % sensitivity of X-ray powder diffraction method).

Magnetization measurements on approximately 40mg quasi-spherical samples, hereafter referred to as "bulk", were carried out in a Quantum Design VSM for temperatures ranging from

100-240 K and at field sweep rates of 0.5 T/min. Slower field sweep rates close to T_c (where the field hysteresis, $H_c^{\uparrow}$-$H_c^{\downarrow}$, is larger), confirmed that any hysteresis seen was intrinsic to the material system, and not a result of non-isothermal conditions due to the magnetocaloric effect itself.[25] The magnetic data were corrected for demagnetization effects with a demagnetization factor, N=0.33.

Microcalorimetry measurements were performed on a 100 μm fragment taken from the bulk sample (m=2.6±0.2 μg) using a commercial Xensor (TCG 3880) SiN membrane chip adapted to work either as an ac calorimeter[26] or as an adiabatic temperature probe[27,28] in a cryostat capable of B = 0-8 T, T = 5-295 K.

When operated as an ac calorimeter, as described by Minakov *et al.*,[26] an ac temperature modulation (heating) is applied to a sample held in an exchange gas of He. The sample size is limited to the size of the heater area ~ 100 μm, corresponding to typical sample mass of a few μg. Thermopile junctions located at the sample and 1mm away (~ T_{bath}) measure the phase and amplitude of the resultant thermal modulation with respect to the source signal; the solution of the heat transfer equation yields the heat capacity, C_p. As the ac measurement is a modulation technique it measures C_p alone, and does not measure the latent heat, L.[8] Any latent heat that may occur on first driving the phase transition will be neither repeatable nor reversible on subsequent ac cycles, within the limitations of the technique as described in depth in reference [8].

When operated as an adiabatic temperature probe, as outlined by Miyoshi *et al.*,[27] the He exchange gas is pumped out (to $P<5x10^{-2}$ mbar) and a passive measurement of the temperature change in response to an applied magnetic field (typically swept at a rate of 0.5 T/min) is obtained. For a sharp first order transition, the latent heat appears as a spiked peak as the field passes through the onset field, H_c.[7,27,29] This peak will have a characteristic decay time of ~1 s. For polycrystalline samples with a correlation length (measure of the nucleation volume) of less than 100 μm the transition will manifest as a series of spikes distributed in field as successive regions undergo the transition. The noise floor of this measurement is of the order of 1 μV, equivalent to ~ 10 nJ.

Zero field (relaxation type) heat capacity measurements were carried out on a larger, polished bulk sample (m=12.5± 0.1 mg) using a Quantum Design PPMS as a secondary check of the absolute magnitude of C_p. The scanning method outlined by Lashley *et al.*[30] and Suzuki *et al.*[31] was employed to resolve the peak in the total heat capacity at T_c.

III. INDIRECT DETERMINATION OF LATENT HEAT

For first order phase transitions where the nucleation volume is less than 100 μm, the latent heat response measured by the microcalorimeter becomes distributed in temperature (or field), and so can fall below the resolution of the adiabatic temperature probe. We have established that in these circumstances L can be estimated indirectly from ac calorimetric measurements of C_p (the true heat capacity) by careful accounting of entropy changes.[28]

The contribution of C_p to the total entropy change, $\Delta S_{HC}(T^*)$, on increasing the field from H_1 to H_2 at temperature T* can be written as:[28]

$$\Delta S_{HC}(T^*)_{\Delta H} = \Delta S(T_{ref})_{\Delta H} + \int_{T_{ref}}^{T^*} \frac{C_p(H_2,T) - C_p(H_1,T)}{T} dT - \left(\frac{L(H_1)}{T_c(H_1)} - \frac{L(H_2)}{T_c(H_2)} \right) \quad \left| \quad T^* < T_c(H_1) \right. \tag{1}$$

$$\Delta S_{HC}(T^*)_{\Delta H} = \Delta S(T_{ref})_{\Delta H} + \int_{T_{ref}}^{T^*} \frac{C_p(H_2,T) - C_p(H_1,T)}{T} dT - \left(\frac{L(T)}{T} - \frac{L(H_2)}{T_c(H_2)} \right) \quad \left| \quad T^* > T_c(H_1) \right. \tag{2}$$

where ΔH is the chosen field change (=H_2-H_1), and $L(H_x)$ is the latent heat at field H_x with corresponding transition temperature $T(H_x)$. These equations consist of three terms: the integration constant $\Delta S(T_{ref})$; the integral ∫(ΔC/T)dt; and a correction term K (H_1, H_2) due to any latent heat (L(H,T)) that varies with temperature. The limit of integration, T_{ref}, is a temperature chosen so that the thermodynamic properties are only weakly temperature dependent (i.e. $\Delta S(T_{ref})$ is small); T_{ref} was taken as 220 K here.

To determine the correction term K due to temperature-dependent L, we compare ΔS_{HC} measured below T_c with ΔS_{Max}, the entropy change obtained from magnetometry

measurements using the Maxwell relation (whilst being careful to avoid the integration artifacts due to a first order phase transition).[32]

For the case $T_{ref}>T_c$, by re-arranging equation (1) and setting $\Delta S_{Max}=\Delta S_{HC}$ for T_{comp} (where T_{comp} is a temperature chosen for the comparison such that $T_{comp} \ll T_c$ and taken here as 110 K) the offset between the two measurements, denoted here as $K(H_1,H_2)$, is found, as described by equation (3).

$$K(H_1,H_2)=\left(\Delta S(T_{ref})_{\Delta H}+\int_{Tref}^{Tcomp}\frac{C_p(H_2,T)-C_p(H_2,T)}{T}dT\right)-\Delta S_{Max}(T_{comp})_{\Delta H}$$
$$=\frac{L(H_1)}{T_c(H_1)}-\frac{L(H_2)}{T_c(H_2)} \qquad (3)$$

Notice that equation (3) describes the difference in latent heat at fields H_1 and H_2. This can be used to estimate the latent heat contribution, and we have previously demonstrated the validity of the correction process in a first order manganite with a distributed ΔS_L caused by a high variability in the occupation of the A site.[28] The strength of this technique is that: a) one can determine $\Delta S_L(0T)$ where it might otherwise be uncertain; b) it can be used to determine H_{crit} accurately; and c) it demonstrates explicitly whether a phase transition is first order or not.

IV. IDENTIFYING THE CRITICAL POINT

A. CALORIMETRIC METHOD

The zero field phase transition of $DyCo_2$ is first order.[9] In order to quantify this we first measured C_p using the ac calorimetry probe. The results are shown in the main panel of figure (1). We stress again that the ac technique employed does not sample L directly, and have demonstrated this for several systems previously.[8,28,28,29] The first observation is that the signature enhancement of C_p of the order of 600% is similar to that seen in the $La(Fe_{1-x}Si_x)_{13}$ material system,[6] and it is quickly suppressed when

the magnetic field and temperature are increased. In contrast, Gd (a local moment system which undergoes a continuous phase transition) also shows a large lambda-like change in C_p, but of the order of 100% only.[33] CoMnSi (which is also thought to be a local moment system that undergoes a first order magnetoelastic phase transition) shows a change of C_p at the AFM/FM transition of only 5%, accompanied by a large latent heat.[29] So it is reasonable to describe the change in C_p in $DyCo_2$ as giant and it is interesting that it is similar in magnitude to a previously-studied IEM system: $La(Fe_{1-x}Si_x)_{13}$.[6,8]

The latent heat as measured by the adiabatic probe approaches the limit of its resolution.[28] The left-hand inset to figure (1) shows raw data from the adiabatic temperature probe run at 137.2 K where the heat capacity peak was at its maximum. Although the signal is weak and distributed, it does indicate the presence of a latent heat, supporting the known first order nature of the transition. The temperature dependence of C_p also indicates first order behavior: The right-hand inset of figure (1) shows the S-T plot determined by integrating the total heat capacity, (C_{total}/T) from 10 K. By comparing the change in entropy, S, from 10 K below T_c, to just above T_c the total entropy change in zero field is estimated to be $\Delta S(0T) \sim 7.5$ J kg^{-1} K^{-1}, which is of a similar magnitude to previously reported values.[18,34,35] The change in entropy obtained in this way from C_p alone is $\Delta S_{HC}(0T) = 5 \pm 0.2$ J kg^{-1} K^{-1}. These two measurements suggest that the latent heat contribution to the entropy change at the transition is of the order of 2.5 J kg^{-1} K^{-1}, which is significant.

To determine the latent heat contribution to the total entropy change in 0 T explicitly we first consider the measurement of C_p in detail, as shown in figure (2) where the calculated values of ΔS_{HC} alongside ΔS_{Max} are plotted for several field changes before the correction term, $K(H_1,H_2)$, (defined in equation (3)) is applied. As stated previously, the correction term $K(H_1,H_2)$ is a consequence of temperature-dependent latent heat on the integration of C_p.[28] Thus, the derived values of K(0,H) which saturate for H > 0.4 T (as shown in the inset of figure (2)) indicate a clearly defined critical field, $H_{crit} = 0.4$ T, where the phase transition changes from first order to continuous. From this, the zero field latent heat contribution to the total entropy change was determined as

$\Delta S_L(0T)$ = 2.6±0.5 J kg^{-1} K^{-1}. Notice that the sum of $\Delta S_{HC}(0T)$ and $\Delta S_L(0T)$ is in agreement with the *total* zero field entropy change, $\Delta S(0T)$, of 7.5 J kg^{-1} K^{-1} observed here and elsewhere.[18,34,35]

Herein lies the strength of this technique: not only can we measure ΔS_{0T}, as is often cited in literature, but we can also separate it into the latent heat expelled at the phase transition and the continuous change in heat capacity. This analysis can provide insight into the evolution of these two contributions as we approach a critical point, and also allows direct comparison between the magnitude of L and the size of the associated field (or thermal) hysteresis.

B. MAGNETIZATION METHOD

In 1964 Banerjee put forward a "generalized approach to first and continuous magnetic transitions".[23] He outlined a criterion to distinguish a magnetic transition as first or continuous from magnetic data alone by combining the Bean-Rodbell model[12] with the Landau-Lifshitz thermodynamic theory of continuous phase transitions. The Free Energy expansion is given in equation (4), where H is the applied field and M the magnetization. At T_c, dF/dM = 0, thus by differentiating equation (4) with respect to M and re-arranging we obtain equation (5).

$$F = A/2M^2 + B/4M^4 + C/6M^6 + D/8M^8 + \ldots - HM \qquad (4)$$

$$H/M = A + BM^2 + CM^4 + DM^6 + \ldots \qquad (5)$$

The Banerjee criterion assumes that the higher order terms in equation (4) can be ignored, which is a reasonable assumption at low M^2, thus the coefficients C and D in equations (4) and (5) are set as zero. It follows that if the value of B, defined in equation (5) is negative, the phase transition is first order. It also follows that larger values of |B| indicate a larger energy barrier and thus a 'stronger' first order phase transition. However, this criterion is widely used even though it is difficult to implement correctly for weakly or disordered first order systems in general (where B is either very small or influenced by disorder broadening of the T_c), and inaccurate for itinerant systems such as $DyCo_2$ in particular (where spin fluctuations not considered in the Mean Field Model should be taken into account).

As the mean field approximation (used in the Banerjee criterion and the Bean-Rodbell model[12]), does not allow for fluctuations of moments about their equilibrium values, for itinerant systems an additional correction is required. For example, as the temperature is increased, spin fluctuations act to lower (renormalize) the energy barrier separating two metastable states,[36] which has the impact of driving a weakly first order phase transition (small, but negative B) towards a continuous phase transition. These fluctuations underpin the Free Energy inequality derived for IEM by Shimizu *et al.*:[21,22,37]

$$3/16<AC/B^2<9/20 \qquad (6)$$

When this inequality is satisfied and A>0, C>0, B<0, a stable (first order) IEM transition can occur.

Figure (3) shows that the higher order terms in equation (5) are required to fit the full curve (where the values of A and B were fixed at low M^2 values to minimize the number of free parameters in the fitting routine). We note that for any *S*-shaped *M-H* curves, phenomenological fitting to the 2nd coefficient, B, alone will never yield a good fit. To determine the value of C for use in the inequality of equation (6), A and B were fixed to their values at low M^2 (as for figure (3)), leaving C and D as free parameters in the fit following equation (5). Figure (4) shows the resultant values of AC/B^2 plotted as a function of temperature, with the shaded area indicating the region described by the Shimizu inequality of equation (6). From this we obtain T_{crit} = 138.5±0.5 K. The inset of figure (4) shows the temperature dependence of B, where the often used Banerjee criterion yields T_{crit}<146 K.

V. DETERMINING THE PHASE DIAGRAM FROM HEAT CAPACITY AND MAGNETIZATION DATA

So far we have determined T_{crit} = 138.5±0.5 K from applying the Shimizu criterion to magnetization data and $\mu_0 H_{crit}$ = 0.4±0.1 T from the vanishing of L in microcalorimetric data. There could be some difference between bulk and fragment data as the former incorporates a distribution of T_c but the latter may have only a smaller subset of this distribution. This usually happens in the

systems that are nonstoichiometric, in which compositional gradients may occur at different length scales. Since $DyCo_2$ is a stoichiometric compound, it is most likely that a small fragment should remain representative of the bulk. There might also be a strain relief in the system by the process of fragmentation.[38,39] To check whether bulk and fragment differ, we measured *M-H* loops of a collection of fragments (<100 μm) and compared them to the bulk, as can be seen in figure (5a). As expected, there is no shift in the critical field, H_c, nor decrease in the hysteresis, ΔH, in contrast to other systems where compositional inhomogeneities, poor thermal conductivity and/or strong magneto-structural coupling (strain relief) play a role.[25,39] As such, it seems our estimates of T_{crit} and H_{crit} are valid for both bulk and fragmented samples.

Figure (5a) also shows the critical field, H_c, determined from the mid-point of the bulk *M-H* loops, where $M=M_{PM}+(M_{PM}-M_{FM})/2$, M_{PM} is the moment of the paramagnetic (PM) phase, and M_{FM} is the moment of the ferromagnetic (FM) phase at H_c. The phase diagram determined this way is given in figure (5b). Note that the uncertainty in $\mu_0 H_c$ is limited to 0.035T by both the time constant of the lock-in used and the chosen field sweep rate, and will increase as the *M-H* loop broadens as is indicated by the error bars of figure (5b). The inset of figure (5a) shows the hysteresis, $\Delta H= H_c^{\uparrow}-H_c^{\downarrow}$, determined from these critical fields with a combined error producing a baseline as indicated of 0.05T.

Also shown in figure (5b) is the trajectory of the peak in C_p measured by ac calorimetry, C_{peak}. The subtlety of the field dependence of C_{peak} is that it approaches the magnetically-determined phase line as the first order behavior vanishes, determined here as T_{crit} = 138.5 K. These observations indicate that the magnetic behavior of $DyCo_2$ is consistent with the Shimizu inequality, as expected for an itinerant system.

VI. DISCUSSION

It is important to compare our results to those found in the literature. As previously mentioned, the Bean-Rodbell model is a mean field (approximation) method that describes the

relationship between the volume change and order of the phase transition based on magnetoelastic coupling in the system.[12] One outcome of this model is the quantity η:

$$\eta = \frac{40 N k_B \kappa T_0 \beta^2 j^2 (j+1)^2}{(2j+1)^4 - 1} \qquad (7)$$

where j is the spin quantum number (= 0.5 for Co and 5 for Dy); $\beta = (T_c/T_o - 1)*(V_o/(V-V_o))$ and T_o and V_o are the volume and Curie temperature in the absence of exchange interaction, respectively; κ is the isothermal compressibility; and N is the number of magnetic carriers per unit volume. If η >1 then the phase transition is considered first order by this model. For example, the model was applied to the ideal $La(Fe,Si)_{13}$ system to demonstrate the relationship between volume change at the transition and magnetic exchange.[40] The $La(Fe,Si)_{13}$ system is ideal because at the phase transition there is a volume expansion of the cubic lattice (no change of symmetry), and the only contribution to the total magnetic moment comes from the Fe atoms (2 μ_B per Fe atom). By substituting Si for Fe the phase transition is driven from first order to continuous, and it was shown by application of this model that a continuous phase transition could still exist when accompanied by some volume change.[40] Unfortunately such a simple comparison is not possible for $DyCo_2$ as: (a) the system is composed of two sublattices of Dy and Co acting in opposition (ferrimagnet); and (b) a cubic-tetragonal distortion occurs at the phase transition, with opposing changes in the lattice parameters *a* and *c* resulting overall in a lower volume change.[17] Clearly, the Bean-Rodbell model is not readily applicable to this system, so we instead formulate a qualitative assessment of its behavior.

The in-field XRD measurements presented by Pecharsky *et al.*,[17] showed a clear discontinuity in the lattice parameters at T_c (H = 0T), which indicates first order character, whereas by 4 T the volume change was observed to be continuous with temperature. These observations are consistent with magnetostriction data (for fields as high as 15 T) that indicated that the field-driven lattice distortion persists to high fields.[41]

Herrero *et al.*[18] used differential scanning calorimetry (DSC) to examine the magnetic phase transitions in a number of $RECo_2$ compounds. For $DyCo_2$ they report a large peak in the DSC scans that persists in magnetic fields of up to 1.5 T; they attributed this peak to the latent heat associated with a first-order transition, despite commenting that they see no indication of any hysteresis. The apparent discrepancy between our two reports lies, however, in the interpretation of the term "latent heat". Where we separate large background changes in the heat capacity across the transition (from a latent heat associated with a hysteretic process), DSC is incapable of distinguishing a peak in the heat capacity - as is often present at continuous phase transitions - from a true latent heat (indicative of a first order transition). Consequently, the DSC measurements provide no evidence of the first-order transition in $DyCo_2$ persisting above the critical field of 0.4T that we infer.

VII. CONCLUSION

Here we confirm explicitly that in zero field the Laves compound $DyCo_2$ exhibits a first order phase transition, but it is quickly suppressed by applied field.[17] Using a newly-developed extension of the microcalorimetry technique in conjunction with magnetic data and the Maxwell relation, we estimate the zero field latent heat contribution (to the total $\Delta S(0T) = 7.5$ J kg^{-1} K^{-1}) of $\Delta S_L(0T) = 2.6\pm0.5$ J kg^{-1} K^{-1}, and the field above which $\Delta S_L = 0$ as $\mu_0 H_{crit} = 0.4\pm0.1$ T, corresponding to $T_{crit} = 138.5\pm0.5$ K. These critical field and temperature values are consistent with those extracted from independent magnetization data using the Shimizu criterion, thus defining the critical parameters conclusively. We also note a striking similarity between $DyCo_2$ and the itinerant system $La(Fe,Si)_{13}$, where although the latent heat is a significant fraction of the total entropy change, the hysteresis is still relatively low, and that both systems show a large and characteristic enhancement of C_p which may be associated with the spin fluctuation contribution at the transition.

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FIGURES

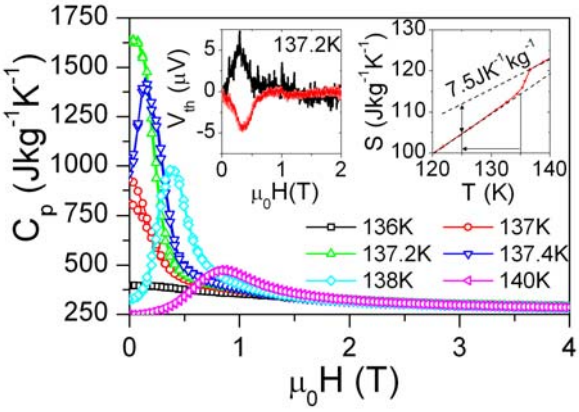

FIG. 1. (Color online) Heat capacity as a function of field at selected temperatures about T_c for both field increase and decrease. C_{peak}~1650 Jkg^{-1}K^{-1} at T=137.2 K, μ_0H=0 T, almost 7 times larger than $C_p(T>T_c)$. Inset left: Signature of distributed latent heat measured at 137.2 K. Inset right: S-T plot determined by integrating the zero field total heat capacity from 10K.

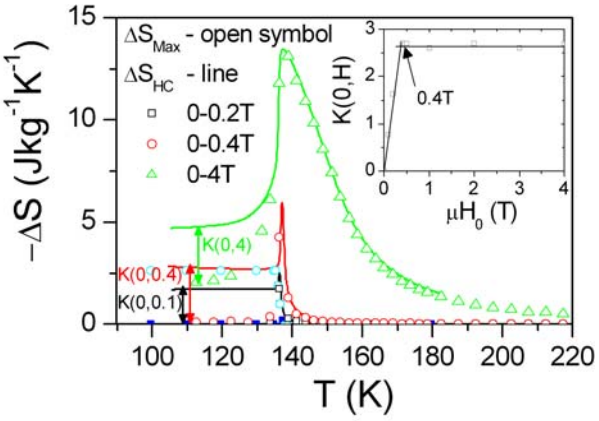

FIG. 2. (Color online) Entropy change ΔS_{HC} calculated by integrating C_p from T_{ref}=220 K. The offset in ΔS_{HC} compared to ΔS_{Max} below T_c (~135 K), is an indication of the temperature dependent latent heat ΔS_L. Inset shows this offset, K(0,H) (in same units Jkg^{-1}K^{-1}), plotted as a function of the critical field and indicates $\Delta S_L(0T)$=2.6±0.5 J kg^{-1} K^{-1}.

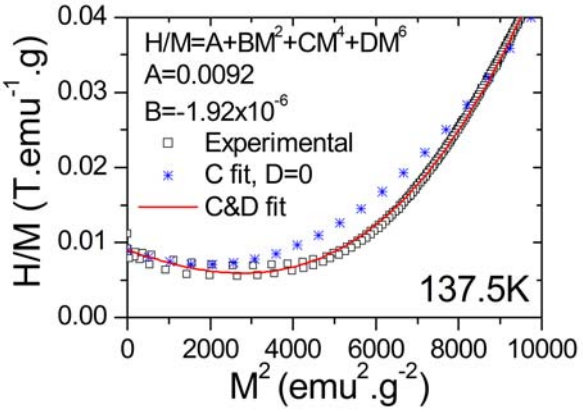

FIG. 3. (Color online) Landau fit at 137.5 K for $DyCo_2$ where parameters A and B, as defined in the text, are fixed at values determined as M^2 approaches zero. Similarly poor fits were observed for other temperatures ($T>T_c$) when parameter D was set to zero.

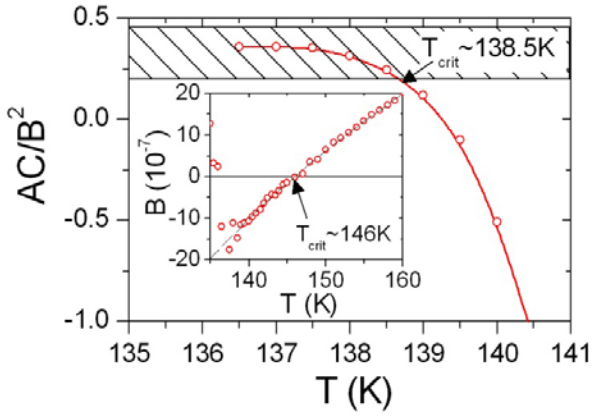

FIG. 4. (Color online) Stability of itinerant metamagnetic behavior as a function of temperature. The hashed area indicates possible values for stable first order IEM as defined by the Shimizu inequality given in the text. The data shown here indicates T_{crit}~138.5 K. Inset shows value of B as a function of temperature where B<0 for T<146 K indicating by the Banerjee criterion that T_{crit}<146 K.

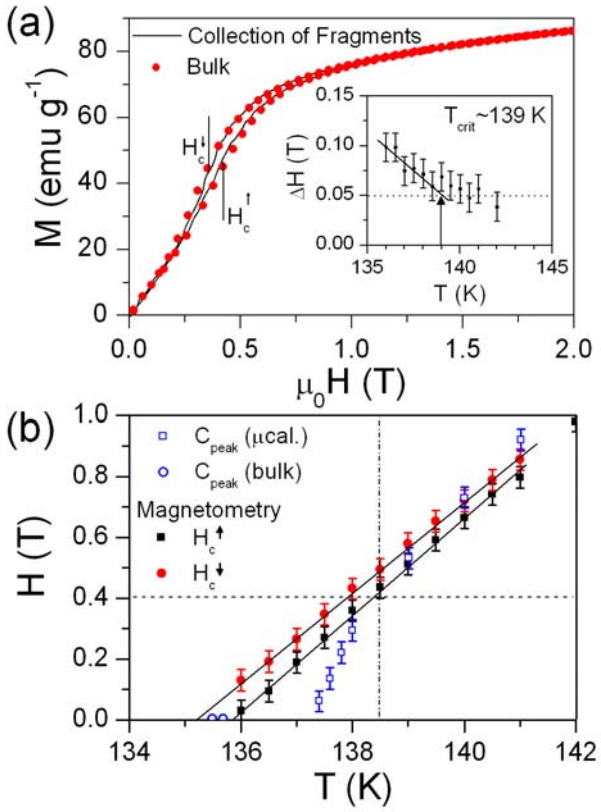

FIG. 5. (Color online) (a) Example bulk and fragment *M-H* loop at 138K. Inset shows hysteresis ($\Delta H=H_c^{\uparrow}-H_c^{\downarrow}$) as a function of temperature where the 0.05T is a minimum baseline due to experimental artifacts. (b) Critical field, H_c, determined from bulk magnetometry and position of the heat capacity peak, C_{peak}, from bulk- and microcalorimetry data. The position of the ac heat capacity peak is the same (within symbol size) for field increase and decrease (as shown in figure (1)). The dashed lines indicate the T_{crit} and H_{crit} as determined by magnetometry and calorimetry respectively. The field and temperature at which hysteresis approaches zero (see inset of (a)) and C_{peak} approaches the bulk phase line, corresponds to H_{crit}=0.45 T and T_{crit}=138.5 K.

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