Identifying the critical point of the weakly first-order itinerant magnet DyCo2 with complementary magnetization and calorimetric measurements

This item was submitted to Loughborough University’s Institutional Repository by the/an author.

Citation: MORRISON, K. ... et al., 2013. Identifying the critical point of the weakly first-order itinerant magnet DyCo2 with complementary magnetization and calorimetric measurements. Physical Review B, 87 (13), 6pp.

Additional Information:

- This article has been published in the journal, Physical Review B [© American Physical Society]. The definitive version is available at: http://link.aps.org/doi/10.1103/PhysRevB.87.134421

Metadata Record: https://dspace.lboro.ac.uk/2134/12651

Version: Published

Publisher: © American Physical Society

Please cite the published version.
Identifying the critical point of the weakly first-order itinerant magnet DyCo$_2$ with complementary magnetization and calorimetric measurements

K. Morrison,$^{1,3}$ A. Dupas,$^1$ Y. Mudryk,$^2$ V. K. Pecharsky,$^2$ K. A. Gschneidner,$^2$ A. D. Caplin,$^1$ and L. F. Cohen$^1$

$^1$The Blackett Laboratory, Imperial College, London SW7 2BZ, UK
$^2$Ames Laboratory, U.S. Department of Energy and Department of Materials Science and Engineering, Iowa State University, Ames, Iowa, 50011-3020, USA
$^3$Department of Physics, Loughborough University, Loughborough, LE11 3TU, UK

(Received 31 May 2012; published 25 April 2013)

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 ferromagnetic 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 magnetic field, $H_{\text{crit}} = 0.4 \pm 0.1$ T and temperature $T_{\text{crit}} = 138.5 \pm 0.5$ K, and we compare these values to those 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.

DOI: 10.1103/PhysRevB.87.134421
PACS number(s): 75.30.Sg, 75.30.Kz, 75.40.−s, 75.50.Cc

I. INTRODUCTION

With recent interest in first order magnetic phase transitions for room-temperature refrigeration,$^{1–3}$ certain classes of materials have generated much attention. In particular, the cubic NaZn$_{13}$-type La(Fe,Si)$_{13}$ (Ref. 4) and the hexagonal Fe$_2$P-type Mn$_{1−x}Fe_{1.95−x}P_{1−y}Si_y$ (Ref. 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,$^{6–8}$ whereas Mn$_{1−x}Fe_{1.95−x}P_{1−y}Si_y$ 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.

Here, $R$Co$_2$ (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 ($7.05 \text{ Å} < a < 7.22 \text{ Å}$)$^{6,11}$ 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$^{3,15}$ and observed by x-ray diffraction (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 magnetic field–temperature ($H$-$T$) phase diagram are much less established, and the critical point (where the first order transition disappears) has not previously been determined.$^{18–20}$

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.$^6$ 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 $H_{\text{crit}}$ and temperature $T_{\text{crit}}$ 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 the U.S. Department of Energy, and major impurities (in atomic parts per million) 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 (1) compensate for the weight loss of Dy during arc melting and (2) prevent the formation of the congruently melting DyCo$_3$. 

DOI: 10.1103/PhysRevB.87.134421 PACS number(s): 75.30.Sg, 75.30.Kz, 75.40.−s, 75.50.Cc

©2013 American Physical Society
phase (a common impurity in DyCo$_2$, which forms from DyCo$_3$ and liquid by a peritectic reaction). An ~8-g button was remelted three 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 d. 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 the x-ray powder diffraction method).

Magnetization measurements on approximately 40 mg quasishperical samples, hereafter referred to as “bulk”, were carried out in a Quantum Design vibrating sample magnetometer (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 nonisothermal conditions due to the magnetocaloric effect itself. 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 ($m = 2.6 \pm 0.2$ μg) using a commercial Xensor (TCG-3880) SiN membrane chip adapted to work either as an ac calorimeter or as an adiabatic temperature probe and 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., 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 a typical sample mass of a few micrograms. Thermopile junctions located at the sample and 1 mm 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 $L$. Any latent heat that may occur on first driving $T_c$ is obtained. For a sharp first order transition, the latent heat appears as a spiked peak as a function of 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 compared $\Delta S_{HC}$ measured below $T_c$ with $\Delta S_{Max}$, the entropy change obtained from magnetometry measurements using the Maxwell relation (while being careful to avoid the integration artifacts due to a first order phase transition). For the case $T_{ref} > T_c$, by rearranging Eq. (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 Eq. (3):

$$K(H_1, H_2) = \left[\Delta S(T_{ref})_{\Delta H} + \int_{T_{ref}}^{T_{comp}} \frac{C_p(H_2, T) - C_p(H_1, T)}{T} dT\right]$$

$$- \Delta S_{Max}(T_{comp})_{\Delta H} = \frac{L(H_1)}{T_c(H_1)} - \frac{L(H_2)}{T_c(H_2)}.$$  (3)

Notice that Eq. (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 $\Delta S_L$ caused by a high variability in the occupation of the A site.\textsuperscript{28} The strength of this technique is that: (1) one can determine $\Delta S_L(0 \text{T})$ where it might otherwise be uncertain; (2) it can be used to determine $H_{\text{crit}}$ accurately; and (3) 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.\textsuperscript{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 Fig. 1. We stress again that the ac technique employed does not sample $L$ directly and have demonstrated this for several systems previously.\textsuperscript{8,28,29} The first observation is that the signature enhancement of $C_p$, the order of 600%, is similar to that seen in the La(Fe$_{1-x}$Si$_x$)$_{13}$ material system,\textsuperscript{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.\textsuperscript{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 antiferromagnetic/ferromagnetic (AFM/FM) transition of only 5%, accompanied by a large latent heat.\textsuperscript{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$_x$)$_{13}$.\textsuperscript{6,8}

The latent heat as measured by the adiabatic probe approaches the limit of its resolution.\textsuperscript{28} The left-hand inset to Fig. 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 Fig. 1 shows the $S-T$ plot determined by integrating the total heat capacity ($C_{\text{total}}/T$) 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 $\Delta S(0 \text{T}) \sim 7.5 \text{ Jkg}^{-1}\text{K}^{-1}$, which is of a similar magnitude to previously reported values.\textsuperscript{18,34,35} The change in entropy obtained in this way from $C_p$ alone is $\Delta S_{\text{HC}}(0 \text{T}) = 5 \pm 0.2 \text{ Jkg}^{-1}\text{K}^{-1}$. These two measurements suggest that the latent heat contribution to the entropy change at the transition is of the order of 2.5 $\text{ Jkg}^{-1}\text{K}^{-1}$, 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 Fig. 2 where the calculated values of $\Delta S_{\text{HC}}$ alongside $\Delta S_{\text{Max}}$ are plotted for several field changes before the correction term $K(H_1, H_2)$ (defined in Eq. (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 $C_p$.\textsuperscript{28} Thus, the derived values of $K(0, H)$ which saturate for $H > 0.4 \text{T}$ (as shown in the inset of Fig. 2) indicate a clearly defined critical field $H_{\text{crit}} = 0.4 \text{T}$ 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 $\Delta S_L(0 \text{T}) = 2.6 \pm 0.5 \text{ Jkg}^{-1}\text{K}^{-1}$. Notice that the sum of $\Delta S_{\text{HC}}(0 \text{T})$ and $\Delta S_L(0 \text{T})$ is in agreement (within error) with the total zero-field entropy change $\Delta S(0 \text{T})$ of 7.5 $\text{ Jkg}^{-1}\text{K}^{-1}$ observed here and elsewhere.\textsuperscript{18,34,35}

Herein lies the strength of this technique: Not only can we measure $\Delta S_{\text{HT}}$, 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”.\textsuperscript{23} He outlined a criterion to distinguish a magnetic transition as first order or continuous from magnetic data alone by combining the Bean–Rodbell model\textsuperscript{12} with the Landau–Lifshitz

![FIG. 1. (Color online) Heat capacity as a function of field at selected temperatures about $T_c$ for both field increase and decrease; $C_p \approx 1650 \text{ Jkg}^{-1}\text{K}^{-1}$ at $T = 137.2 \text{ K}$, $\mu_0 H = 0 \text{ T}$, 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 10 K.](image1)

![FIG. 2. (Color online) Entropy change $\Delta S_{\text{HC}}$ calculated by integrating $C_p$ from $T_{\text{ref}} = 220 \text{ K}$. The offset in $\Delta S_{\text{HC}}$ compared to $\Delta S_{\text{Max}}$ below $T_c$ ($\sim 135 \text{ K}$), is an indication of the temperature dependent latent heat $\Delta S_L$. Inset shows this offset $K(0, H)$ (in same units, Jkg$^{-1}\text{K}^{-1}$) plotted as a function of the critical field and indicates $\Delta S_L(0 \text{T}) = 2.6 \pm 0.5 \text{ Jkg}^{-1}\text{K}^{-1}$.](image2)
thermodynamic theory of continuous phase transitions. The free energy expansion is given in Eq. (4), where $H$ is the applied field and $M$ the magnetization. At $T_c$, $dF/dM = 0$, thus by differentiating Eq. (4) with respect to $M$ and rearranging, we obtain Eq. (5):

$$F = A/2M^2 + B/4M^4 + C/6M^6 + D/8M^8 + \cdots - HM.$$  \hspace{1cm} (4)

$$H/M = A + BM^2 + CM^4 + DM^6 + \cdots$$  \hspace{1cm} (5)

The Banerjee criterion assumes that the higher-order terms in Eq. (4) can be ignored, which is a reasonable assumption at low $M^2$; thus, the coefficients $C$ and $D$ in Eqs. (4) and (5) are set as zero. It follows that, if the value of $B$, defined in Eq. (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, an additional correction is required for itinerant systems. 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.:$^{21,37}$

$$3/16 < AC/B^2 < 9/20.$$  \hspace{1cm} (6)

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

Figure 3 shows that the higher-order terms in Eq. (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 second coefficient $B$ alone will never yield a good fit. To determine the value of $C$ for use in the inequality of Eq. (6), $A$ and $B$ were fixed to their values at low $M^2$ (as for Fig. 3), leaving $C$ and $D$ as free parameters in the fit following Eq. (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 Eq. (6). From this, we obtain $T_{\text{crit}} = 138.5 \pm 0.5$ K. The inset of Fig. 4 shows the temperature dependence of $B$, where the often-used Banerjee criterion yields $T_{\text{crit}} < 146$ K.

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

So far, we have determined $T_{\text{crit}} = 138.5 \pm 0.5$ K from applying the Shimizu criterion to magnetization data and $H_{\text{crit}} = 0.4 \pm 0.1$ 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 ($<100$ $\mu$m) and compared them to the bulk, as can be seen in Fig. 5(a). As expected, there is neither a shift in the critical field $H_c$ nor a decrease in the hysteresis $\Delta H$, in contrast to other systems where compositional inhomogeneities, poor thermal conductivity, and/or strong magnetostructural coupling (strain relief) play a role.$^{25,39}$ As such, it seems our estimates of $T_{\text{crit}}$ and $H_{\text{crit}}$ are valid for both bulk and fragmented samples.

Figure 5(a) also shows the critical field $H_c$, determined from the midpoint 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 FM phase at $H_c$. The phase diagram determined this way is given in Fig. 5(b).
One outcome of this model is the quantity $\eta$:

$$\eta = \frac{40Nk_B\kappa T_0\beta^2 j^2(j+1)^2}{(2j+1)^4-1}, \quad (7)$$

where $j$ is the spin quantum number ($= 0.5$ for Co and $5$ for Dy); $\beta = (T_c/T_0 - 1)[V_o/(V - V_o)]$ and $T_o$ and $V_o$ are the Curie temperature and the volume in the absence of an exchange interaction, respectively. $\kappa$ is the isothermal compressibility; and $N$ is the number of magnetic carriers per unit volume. If $\eta > 1$, 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. 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 $\mu_B$ 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.

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. 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. showed a clear discontinuity in the lattice parameters at $T_c$ ($H = 0$ T), 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.

Herrero et al. used differential scanning calorimetry (DSC) to examine the magnetic phase transitions in a number of RCo$_2$ 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 0.4 T that we infer.

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. 

VII. CONCLUSION

Here, we confirm explicitly that in zero field, the Laves phase compound DyCo$_2$ exhibits a first order phase transition, but it is quickly suppressed by applied field. 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 \( \Delta S(0T) = 7.5 \text{ Jkg}^{-1} \text{K}^{-1} \)] of \( \Delta S_l(0T) = 2.6 \pm 0.5 \text{ Jkg}^{-1} \text{K}^{-1} \), and the field above which \( \Delta S_l = 0 \) as \( H_{	ext{cur}} = 0.4 \pm 0.1 \text{ T} \), corresponding to \( T_{	ext{cur}} = 138.5 \pm 0.5 \text{ K} \). 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 DyCo2 and the itinerant system LaFeSi13, 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 flip transition at the transition.

ACKNOWLEDGMENTS

The research leading to these results has received funding from the European Community’s 7th Framework Programme under Grant Agreement No. 214864 (“SSEECC”) and EPSRC EP/G060940/1. The sample preparation and x-ray characterization were performed at the Ames Laboratory of the U.S. Department of Energy. Work at Ames Laboratory is supported by the Office of Basic Energy Sciences, Materials Sciences Division of the Office of Science, U.S. Department of Energy. The Ames Laboratory is operated by Iowa State University of Science and Technology for the U.S. Department of Energy under Contract No. DE-AC02-07CH11358.