Novel Thermal Effects at the First Order Magnetic Phase Transition in Erbium, and a Comparison with Dysprosium

K. A. Gschneidner, Jr. and V. K. Pecharsky
Ames Laboratory and Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011-3020

David Fort
School of Metallurgy and Materials, University of Birmingham, Birmingham, B15 2TT, United Kingdom

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In low temperature studies of ultrapure erbium (and dysprosium) we have discovered unusual thermal effects at the first order magnetic transformation of erbium ($\cong$19 K). These include (1) superheating (i.e., *the metal is colder after heat has been added to it than before the heat pulse*), (2) supercooling, and (3) the existence of metastable intermediate phases during this phase transformation in erbium (four on heating and two on cooling). In comparison, dysprosium exhibits both superheating and supercooling, but no intermediate metastable phases are observed. Furthermore, none of these effects are observed in less pure metals. [S0031-9007(97)03295-X]

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In spite of the fact that the magnetic and thermal properties of erbium (and also dysprosium) have been extensively studied for about 40 years [1–7], recent measurements of ultrapure electrotransport purified lanthanide metals have revealed some unique behaviors associated with the first order magnetic transition of erbium ($T_c \cong 19$ K). These novel thermal effects include (1) *the cooling of erbium when heat has been added to it* at the Curie point, i.e., superheating; (2) *the warming of erbium when heat is being removed from the sample*, i.e., supercooling; and (3) the observation of metastable intermediate phases during this first order magnetic phase transformation (four on heating and two on cooling). The results of these new measurements are described below. In addition, we have compared the behavior of erbium with those of dysprosium at its first order magnetic transition ($T_c \cong 90$ K).

The magnetic phase transitions in the heavy lanthanides were first observed about 40 years ago by Spedding and Legvold and their colleagues [1–4]. Since then, hundreds of papers have been published, e.g., see Refs. [5–7]. But two developments in the past five years have made it possible to observe new thermal phenomena at the first order transitions of dysprosium [8] and erbium. The first was the availability of ultrahigh purity metals prepared by a combination of sublimation (at Ames) and solid state electrolysis (SSE) (at Birmingham) of the best routinely prepared Ames Laboratory rare earth metals [9]. The second was the design and construction of a semiadiabatic fully automated calorimeter with a *very low mass addenda* to measure heat capacities from 3.5 to 350 K in 12 to 15 h [10]. Although the low temperature heat capacity of SSE erbium had been measured from 1.5 to 80 K by us four years ago [11], we did not detect these thermal effects because the mass of the earlier calorimeter was about 5 times that of the newer calorimeter, and this mass masked the delicate and weak anomalies.

The main reason for reexamining the heat capacity of erbium was to see if the superheating effect observed in dysprosium [8] also occurred in erbium, especially to see if the crystal structure change in dysprosium may have been responsible for this thermal phenomenon. The high degree of purity of polycrystalline dysprosium leads to quite an unusual thermal effect [8]: the transformation proceeds through the bulk of the material causing the temperature to drop abruptly, i.e., during the heat pulse the ultrapure dysprosium cools down as a result of adding heat. As is seen in the individual heat pulse measurements (Fig. 1), superheating also occurs in ultrapure erbium—as shown in Fig. 1(b)—where the erbium sample initially warms to 19.03 K and then cools down to 18.87 K which is lower than the temperature (18.92 K) at which the heat pulse was started. Note that there is a natural temperature drift (increase) between the beginning and the end of the heat pulse due to the equilibrium heat exchange between the calorimeter and the surroundings (Fig. 1) and, hence, the resulting temperature drop is indeed larger (it approaches a total decrease of 0.15 K) after correcting for this drift. Normal heat pulses just below and just above the transition are shown in Figs. 1(a) and 1(c), respectively.

It is known that the crystal structure of dysprosium changes from the normal close-packed hexagonal structure to an orthorhombic (slightly distorted hexagonal) structure upon cooling through the 90 K magnetic transformation [12]. In contrast, no crystal structure change occurs in erbium at ~19 K, but there is a large expansion of the c-axis lattice parameter upon cooling through this transition [13]. Clearly, the crystal structure change is not a necessary condition for the existence of the superheating effect. However, in both materials there is a large change in at least one of the lattice parameters during these first order magnetic transformations: for erbium an expansion in the c axis of 0.36% upon cooling [13], with a small

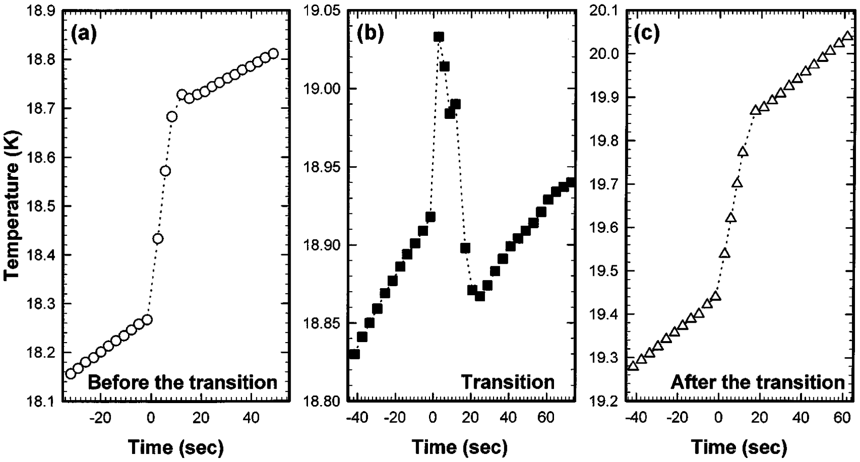

FIG. 1. The time-temperature behavior during heat pulse measurements near the first order magnetic phase transition of erbium for three successive heat pulses.

contraction in the basal plane of ~0.01% [14], while for dysprosium (in terms of the low temperature orthorhombic lattice) a contraction of 0.48% along b, and expansions of 0.22% along a and 0.19% along c [12], also upon cooling.

The heat capacity of SSE purified erbium from 3.5 to 100 K is shown in Fig. 2(a). For comparison, that of SSE purified dysprosium is shown in Fig. 2(b). The magnetic behavior, and, hence, the heat capacity which is the sum of the electronic, lattice, and magnetic heat capacities, of erbium is more complex than that of dysprosium. Two major second order transformations occur at ~84 K [paramagnetic (P) to a c-axis modulated ferromagnetic (CAM)] and at ~52 K [CAM to a complex magnetic structure-antiphase domain + cone + helix (APD)]; and a first order transition is observed at ~19 K [APD to a ferromagnetic cone + helix (FC)], plus several spin-slip transitions [the most obvious one, Fig. 2(a), occurs at ~25 K]. In comparison, dysprosium exhibits a second order transformation at ~180 K [P to antiferromagnetic helical (H)] and a first order transition at ~90 K [H to ferromagnetic (F)]. We will be concerned with only the first order transformations, and it is immediately obvious that the ~19 K erbium transition has a finite width, while the 90 K dysprosium transition is infinitely narrow. In fact, ultrapure Dy may be the only metallic material in which the heat capacity in the vicinity of a first order phase transition behaves exactly as predicted by thermodynamic theory, i.e., it is infinite at $T = T_c$ and has no onsets below and above the transition [8].

Just as for the dysprosium, heating and cooling (time-temperature) curves were taken to verify the existence of superheating and also supercooling in erbium. As seen in Fig. 3(a), superheating does indeed occur, but much to our surprise there are four drops in the temperature as the transformation occurs. This compares to just a single temperature drop for dysprosium [Fig. 3(b)] suggesting that as the erbium transforms from the low temperature FC phase, it goes through four intermediate metastable magnetic states before it forms the stable APD phase above 19 K. Upon cooling, supercooling is observed on going

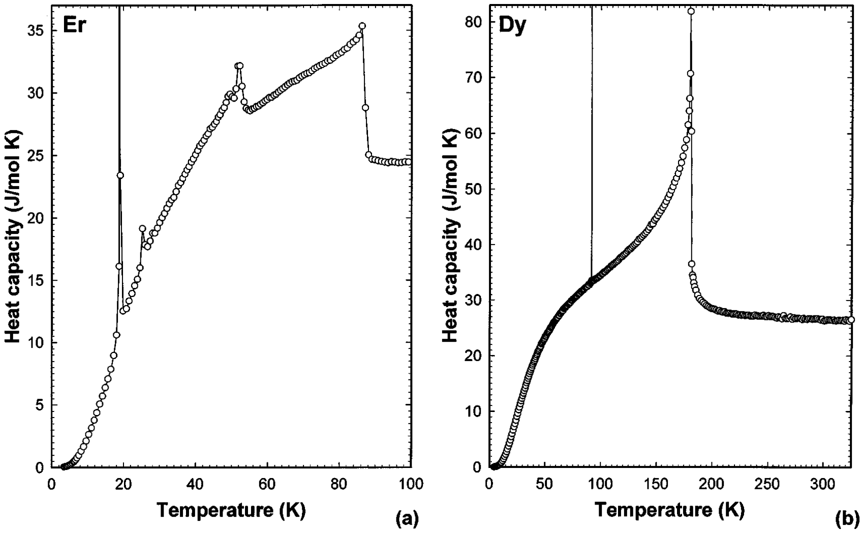

FIG. 2. The heat capacities of erbium from 3.5 to 100 K (a) and dysprosium from 3.5 to 350 K (b).

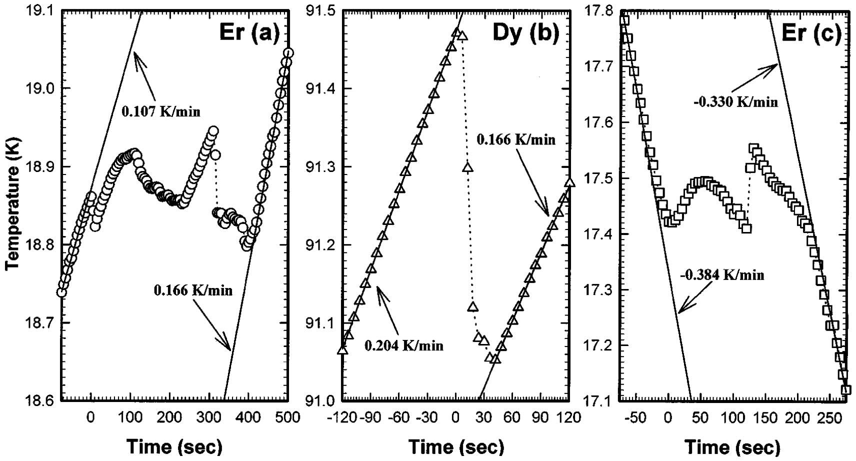

FIG. 3. Time-temperature heating (a), (b) and cooling (c) curves for SSE erbium (a), (c) and SSE dysprosium (b).

from the APD phase to the FC phase, but in this case only two intermediate metastable magnetic structures are clearly observed [Fig. 3(c)], while in dysprosium again no intermediate states are observed [8]. These measurements were repeated on a second SSE purified erbium sample and nearly identical results were obtained; the main difference was that the heights of the peaks varied somewhat between the two runs, which we attribute to the difference in the masses of the two samples and thus the difference in the ratios of the sample mass to the addenda mass of the calorimeter. The reproducibility of the time-temperature behavior was much better when the measurements were repeated using the same sample. It was impossible, however, to obtain two sets of data which matched exactly since warming (cooling) rates were not identical and, hence, the changes in the temperature behavior occur at slightly different times compare to that shown in Figs. 3(a) and 3(c). On the contrary, the time-temperature behavior of ultra pure Dy [Fig. 3(b) and Ref. [8]] is exactly reproducible independent of the warming (cooling) rates.

One will notice that the time span for the respective first order transformations is about 1 order of magnitude larger for erbium than for dysprosium, even though the sample sizes are about the same ($\sim$1 g). This is consistent with the breadth of the first order heat capacity peaks shown in Figs. 2(a) and 2(b).

We have also examined routinely prepared Ames Laboratory (AL) erbium and dysprosium samples, which were 99.85 at. % pure (with 740 ppm atomic interstitial impurities) and 99.9 at. % pure (with 660 ppm atomic interstitial impurities), respectively. This compares with the 99.97 at. % pure (320 ppm atomic interstitial impurities) SSE erbium [9], and 99.96 at. % (310 ppm atomic interstitial impurities) SSE dysprosium [8]. No superheating effects were observed during the heat capacity measurements for either AL metal; however, the heat pulses were anomalous in the vicinity of the 19 K transition in erbium and 91 K transition in dysprosium, but the samples were never colder after the heat pulse than before, in contrast to the behavior shown in Fig. 1(b) for the SSE erbium or SSE dysprosium [8].

As shown in the heating and cooling time-temperature curves [Figs. 4(a) and 4(b), respectively] for the normal AL erbium, there is little evidence, if any, for the existence of these intermediate metastable phases, although knowing what we have observed on the SSE erbium, one might consider that the small peak in the cooling curve at 90 sec [Fig. 4(b)] would be evidence for such a phase.

Although we obtained experimental evidence that superheating and supercooling in ultrapure erbium and dysprosium occurs during the first order magnetic phase transition without or with (respectively) a crystal structure change, it has been noted earlier that magnetoelastic interactions have a strong effect on equilibrium properties of the lanthanide metals, and that the first order phase transition in dysprosium is, in fact, driven by the magnetoelastic energy [15]. Furthermore, it has been experimentally shown that upon lowering the temperature, the increased magnetoelastic strain in the lattice causes the loss of long range magnetic order and ultimately leads to ferromagnetic transitions [16].

The existence of metastable intermediate phases during the first order transition of erbium is not too surprising considering the number of complex magnetic phases that exist, including the various spin-slip transitions in addition to the three main magnetically ordered structures, which are rather exotic. Thus it is not unreasonable that as the antiphase domain + cone + helix phase transforms to the ferromagnetic cone + helix magnetic structure on cooling, the transformation would proceed through two intermediate structures [Fig. 3(c)]. Also, the reverse pathway from the low temperature phase to the high temperature one does not necessarily need to be the same, and so the existence of four intermediate magnetic structures is plausible.

The absence of intermediate states during the first order transition in dysprosium is probably due to the fact that the magnetoelastic energy is much larger in the case of dysprosium compared to that in erbium and, hence, crystal and magnetic structure are strongly coupled. Furthermore,

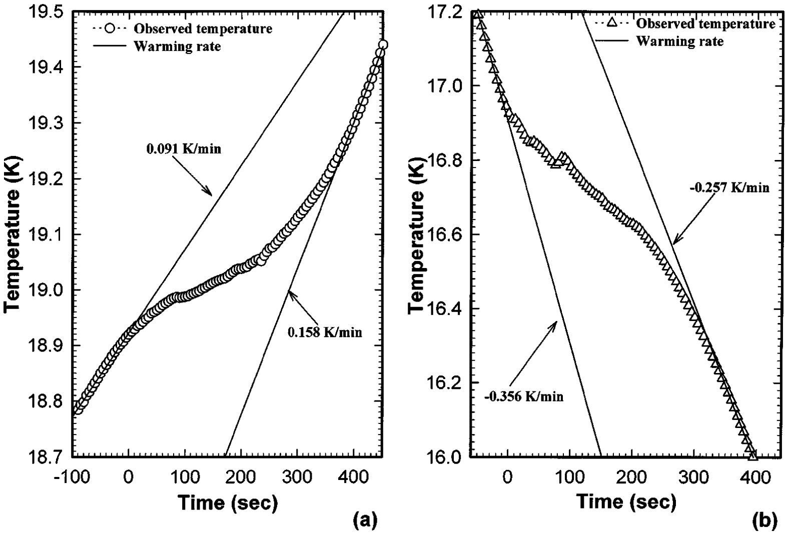

FIG. 4. Time-temperature heating (a) and cooling (b) curves for routinely prepared high purity Ames Laboratory erbium.

both magnetic structures here are quite simple and the transition can proceed directly from one to the other without the need to form an intermediate metastable phase(s). The same is also true in the reverse direction.

The lack of any structure in the heating and cooling curves of the standard AL erbium indicates that impurities play an important role. As noted above, the magnetoelastic strain is, most likely, the ultimate driving force for the occurrence of the first order phase transitions in both erbium and dysprosium. And since the interstitial impurities produce strain fields in the crystal lattice, which interact with the magnetoelastic strain, increasing the impurity contents will have an increasingly larger effect on the net magnetoelastic strain in the metal. In the purer SSE erbium, the low concentration of impurity strain fields allows one metastable structure to transform completely to another one over a short time/temperature interval, allowing us to detect their presence. But in the AL erbium the presence of a large number of impurity strain fields may either prevent a phase from forming or, more likely, slow down the transformation from one metastable state to another, and thus these metastable states tend to coexist and mask out any thermal effects as seen in Figs. 3(a) and 3(c).

The determination of the metastable magnetic structures will present a difficult challenge to the experimentalist because of the narrow temperature ranges (tenths of a degree Kelvin) over which they exist. Furthermore, the existence of these structures may very well be time dependent, and if so, long term neutron diffraction studies may be out of the question.

Our studies have shown that both dysprosium and erbium are the first two materials in which *both* superheating and supercooling have been observed. We have also shown that the first order magnetic transition in erbium takes place via four intermediate metastable phases upon heating and only two such phases on cooling, but no intermediate phases are found in the corresponding first order phase transition in dysprosium. Furthermore, these thermal effects are observed in only ultrapure SSE purified lanthanide metals.

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