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The specific heat of samarium and holmium in the range 2–32 K

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Abstract. Measurements of the specific heat in the temperature range 2–32 K have been made on a high-purity single crystal of holmium and two polycrystalline samples of samarium. Holmium shows a discontinuous transition at 19.46 K with an entropy of $0.14 \pm 0.02 \text{ J mol}^{-1} \text{ K}^{-1}$ and a latent heat of $2.7 \pm 0.3 \text{ J mol}^{-1}$. There is a small peak at 17.3 K. Samarium has a large peak at 13.7 K, a smaller peak at 20.4 K and a very small anomaly at 9.6 K. The size and shape of the peaks depends upon the purity of the sample.

1. Introduction

The magnetic rare-earth metals samarium and holmium undergo several magnetic transitions in the temperature range 5–150 K. In previous studies [1, 2], those transitions that occur above 80 K have been studied by means of specific heat measurements made on some of the relatively pure samples of these elemental metals that have become available in the past decade. In this paper we report results of measurements made on the same samples at lower temperatures between 2 and 32 K.

In holmium the critical behaviour that occurs at the transition from paramagnetism to helical order at 132 K has been analysed in detail by Jayasuriya and co-workers [1], whose measurements were made on a single crystal of 99.91 at.% purity. Recently specific heat measurements on the same single crystal have been made in the region 0.6–5 K [3] and the components of the specific heat due to the hyperfine interaction, electrons, phonons, and magnons, independently, were found to be in reasonable agreement with measurements made a decade earlier on a polycrystalline sample of lower purity [4]. In the temperature range in which a transition occurs from a helical state to a conical spiral (at around 20 K), measurements have been made by Gerstein and co-workers [5] and by Lounasmaa and Sundstrom [6]. Both sets of authors observed one peak; in [5] it was at 19.5 K and reported to depend on thermal history; in [6] a peak was found at 17.5 K but no history dependence was found.

At 105 K rhombohedral samarium undergoes a transition from paramagnetism to a collinear antiferromagnetic state in which only two thirds of the atomic moments are ordered; their direction lies along the *c* axis [7]. Below about 14 K the remaining third

of the moments order, also along the *c* axis. The size of the atomic moments is reduced by a factor of two by itinerant-electron polarisation [8]; the nature of the magnon spectrum is unknown.

Of the earlier investigations of the specific heat of samarium [9–14] those described in [9] (2–30 K), [10] (13–350 K) and [13] (3–25 K) covered the temperature range in which the lower transition takes place. All three measurements showed a large peak at about 14 K, and a small anomaly was found at about 9.5 K. In a recent study [2] of the 105 K transition of samples of samarium of generally higher purity than those used previously [9–11] the 105 K peak was found to be rounded rather than having the cusp observed by Jennings and co-workers [10] in a much less pure sample, although away from the transition reasonable agreement was found with their measurements.

2. Experimental details

The holmium single crystal was the one used in [1]. It had a mass of 28.15 g and a purity of 99.91 at.%, the principal impurities being hydrogen, oxygen, carbon, nitrogen and iron. Two polycrystalline samarium samples from among those examined recently [2] were used. Sample Sm IV was prepared by the Ames Laboratory and was of 99.89 at.% purity (including gaseous impurities); it was dehydrogenated to 0.01 at.% hydrogen at Ames and then heat treated at 550 °C in ultra-high vacuum. Sample Sm V was received as Sublimed Grade from Rare Earth Products and stated to be of 99.98% purity (excluding gaseous impurities) by the supplier; as it was purchased by us before 1980 it is likely to have contained a much higher level of gaseous impurities than modern samples. This sample was consolidated by RF melting on a copper hearth under purified argon [2]. The specific heat measurements were made by a semi-adiabatic heat pulse method [3, 15]. The overall inaccuracy of the measurements is less than $\pm 0.4\%$ below 20 K, but above that temperature the loss of resolution of the germanium resistance thermometer resulted in an increased scatter of the data points. The results obtained for the two rare earths are shown in figures 1–4.

3. Discussion

The specific heat of holmium over our full temperature range is shown in figure 1. The data below 5 K have been analysed in terms of hyperfine, electron, phonon, and magnon terms [3]. Two transitions are seen with peaks at 17.30 and 19.46 K, which appear to correspond, respectively, to those seen in [6] and [5]. Our values of the specific heat are lower than those of Lounasmaa and Sundstrom [6] in the region below the transitions; in the region of the transition they are greater, and above 21 K they agree within 2%. We found no indication in our work that the specific heat depended on thermal history. The peaks are shown over a smaller temperature range in figure 2. The higher-temperature peak extends up to a value of $145 \text{ J mol}^{-1} \text{ K}^{-1}$ at 19.46 K, and between 19.456 and 19.486 K it is off the scales of figures 1 and 2. The narrowness of this peak (0.03 K) suggests that the transition is discontinuous. We have estimated a latent heat for this transition by numerical integration of the area between the experimental points and the straight line A–B that joins the continuous values on either side of the transition. The resulting latent heat is $2.7 \pm 0.3 \text{ J mol}^{-1}$ and the excess entropy $0.14 \pm 0.02 \text{ J mol}^{-1} \text{ K}^{-1}$. The peak we see at 17.3 K is less sharp than that seen by Lounasmaa and Sundstrom [6];

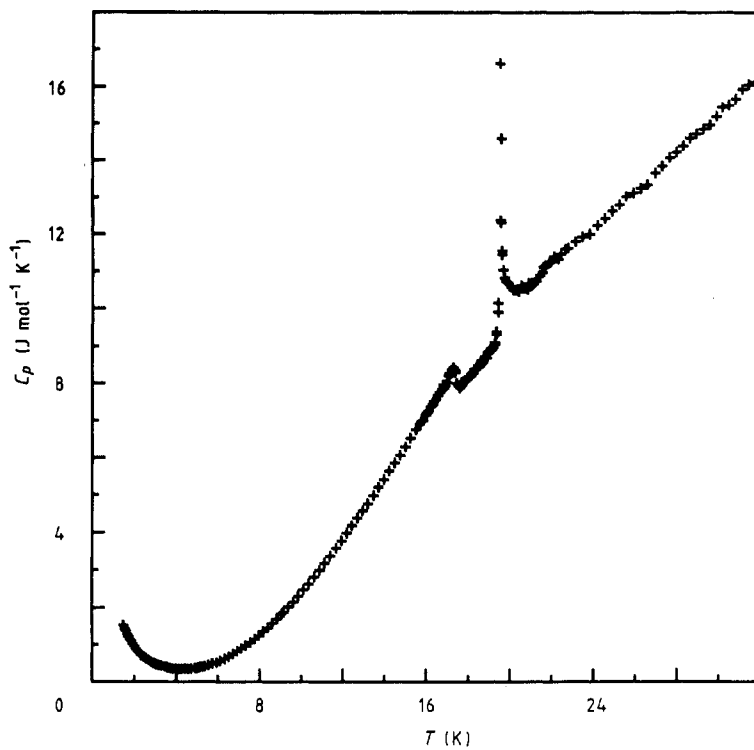


Figure 1. The specific heat, C_p , of holmium in the temperature range 0–32 K.

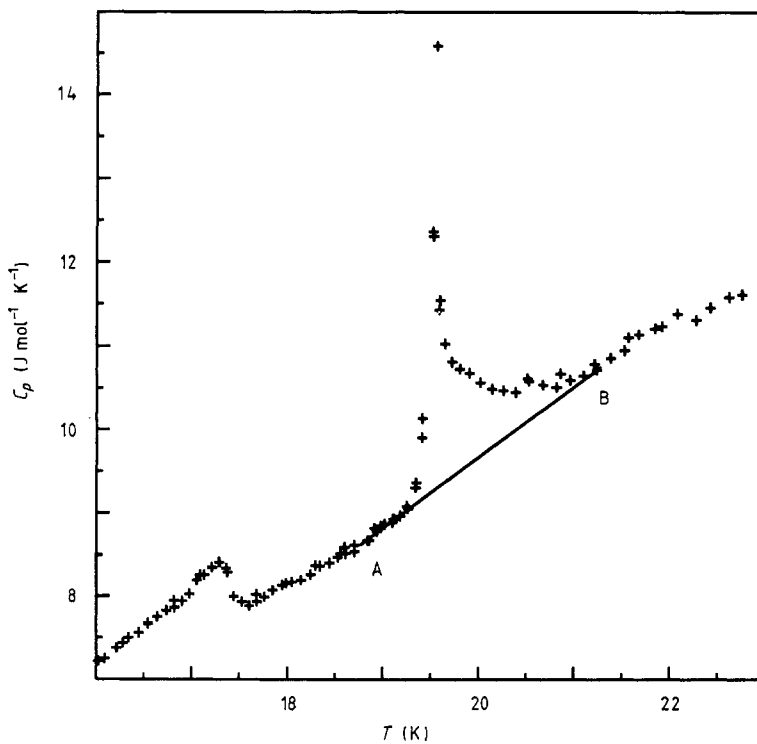


Figure 2. The specific heat, C_p , of holmium in the temperature range 16–23 K.

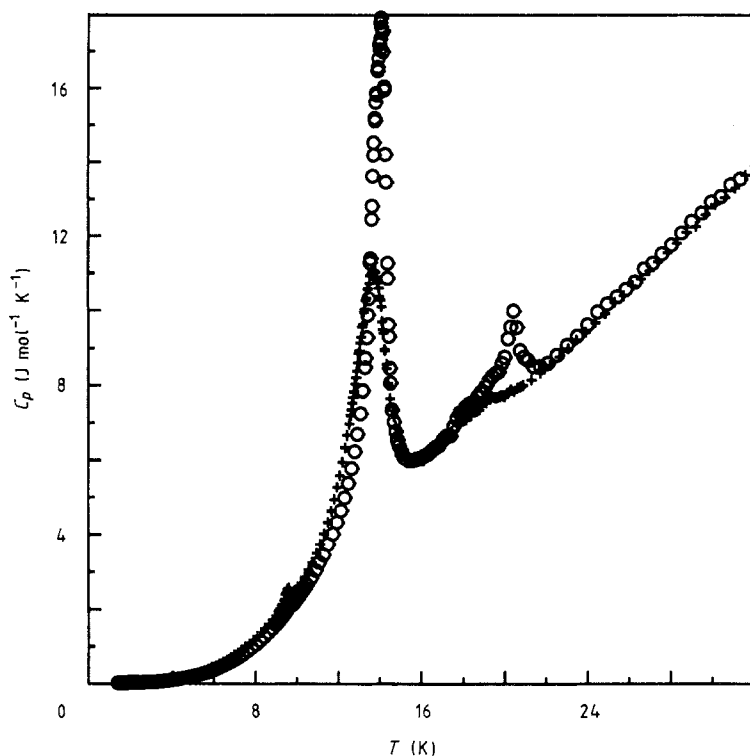


Figure 3. The specific heat, C_p , of the two samarium samples in the temperature range 0–32 K. \circ : Sm IV; +, Sm V.

the excess entropy under this peak between 12.0 and 17.7 K is $0.1 \pm 0.02 \text{ J mol}^{-1} \text{ K}^{-1}$. This may be compared to the value of $0.28 \text{ J mol}^{-1} \text{ K}^{-1}$ found in [6] over the range 9 to 18.2 K. The wider range used by [6] for the integration was inappropriate for our measurements as it gave rise to incremental excess entropies that were negative at the ends of the range.

The peak at 19.46 K is associated with the transition of the spin structure from a flat spiral to a conical spiral [16]; the 17.3 K peak may be associated with some other form of spin reorientation.

The data for our two samarium samples are shown in figure 3. There are three anomalies at 9.6, 13.7 and 20.4 K; the data near the lowest-temperature anomaly are shown in more detail in figure 4. Our data on the purer Sm IV sample were lower than those of [11] up to 13.5 K; above 13.5 K they were higher but the difference decreased to 2% of the values of [11] at 24 K. The lower-purity Sm V had a specific heat intermediate between that of the sample of [11] and of Sm V. The 20.4 K peak, which is prominent in the Sm IV data and which has not, to our knowledge, been reported before, is reduced to a diffuse bump in Sm V and is not visible at all in the data of [11]. This suggests that the samples are, in order of increasing purity, that of [11], Sm V and Sm IV. The effect of increasing impurity content is apparently to smear out and reduce the amplitudes of the upper two transitions. The 9.4 K peak is, though, an exception. In figure 4 and [11] it is seen that as the sample purity increases the peak temperature increases slightly but the peak amplitude decreases. The excess entropy of this peak between 9.0 and 10.0 K is $4 \pm 0.5 \text{ mJ mol}^{-1} \text{ K}^{-1}$; this is ten times smaller than the value found in [11], but as the

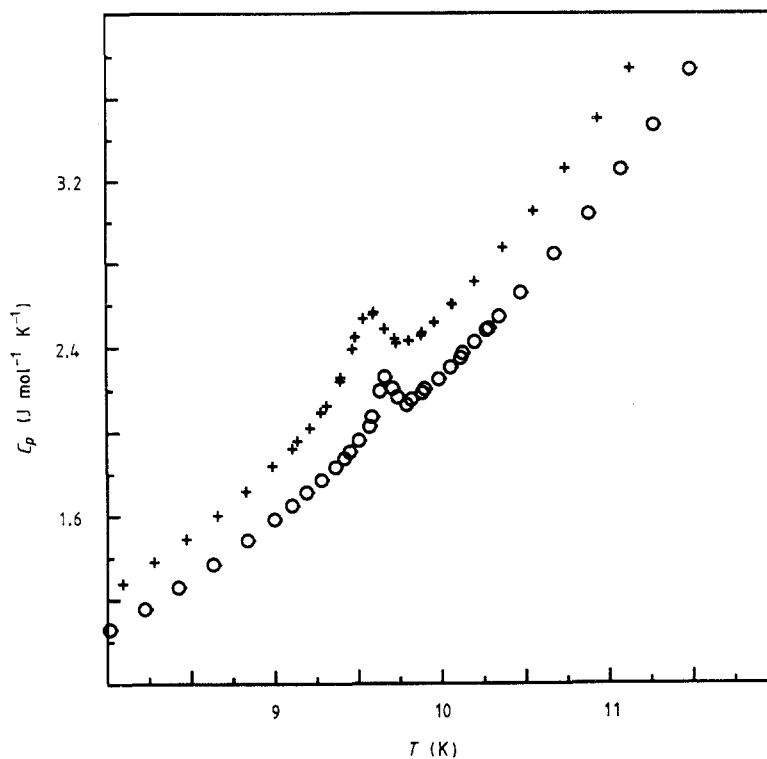


Figure 4. The specific heat, C_p , of the two samarium samples in the temperature range 8–12 K. \circ : Sm IV; +, Sm V.

size of the anomaly in our two samples of substantially differing purity is much the same it is not clear whether this anomaly is an intrinsic one or associated with impurities. The excess entropy of the 13.7 K peak in Sm IV between 10.2 and 17.5 K is $1.14 \pm 0.1 \text{ J mol}^{-1} \text{ K}^{-1}$ and that of the peak at 20.4 K between 17.5 and 23.0 K is $0.114 \pm 0.02 \text{ J mol}^{-1} \text{ K}^{-1}$. By comparison, the entropy associated with the degeneracy of one third of a spin-half system is $1.92 \text{ J mol}^{-1} \text{ K}^{-1}$. The peak at 13.7 K may therefore be associated with the resolution of the degeneracy of the one third of the atoms that order at this temperature [7], but the other two peaks with much lower entropy are presumably associated with reorientation of the spin direction rather than any substantial change in the magnitude of the spin. We note that the larger the sample purity, the higher the 13.7 and 20.4 K peaks—in contrast to the case for the peak at 106 K where the reverse seems to be true [2]. The entropies at, say, room temperature of all the samples may then be the same, despite the differences between their entropies at intermediate temperatures, but measurements of specific heat over a temperature range of at least 2–150 K (above which the specific heats of all the samples agreed [2]) will be needed to confirm this.

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