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1989 J. Phys.: Condens. Matter 1 6987

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Phase transitions and the thermal expansion of holmium

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Received 7 June 1989

Abstract. We have measured the thermal expansion for holmium parallel (\parallel) and normal (\perp) to the c axis. The results confirm that the magnetic transitions at 132 K and 17.3 K are second order while that at 19.5 K is discontinuous (first order). The linear expansions are very anisotropic, α_{\parallel} being large and negative below 100 K while α_{\perp} is large and positive. The data lead to values for the principal Grüneisen parameters of $\gamma_{\parallel} \approx -3$ and $\gamma_{\perp} \approx +2$ below 15 K. The volume coefficient $\beta = 2\alpha_{\perp} + \alpha_{\parallel}$ is comparable with that of normal metals excepting near the magnetic transition. There is no evidence of a significant nuclear hyperfine term in the α -values for holmium.

1. Introduction

The magnetic structure of a heavy rare-earth, holmium, has been discussed recently by Cowley and Bates (1988)—see also Bates *et al* (1988). In brief, holmium orders on cooling first to an incommensurate antiferromagnetic state at $T_N = 132$ K; this is a basal spin spiral in which the magnetic moments are confined to each ferromagnetic plane. On cooling further, at about 19.5 K (hereafter labelled T_c), the magnetic moments tilt out of the basal plane to form a ferromagnetic cone. Then at about 17.3 K (T_R in this paper) a rearrangement of the spins occurs. In addition to neutron studies (see, e.g., Koehler *et al* 1966, Cowley and Bates 1988), there have been numerous calorimetric measurements through these transitions, most recently by Jayasuriya *et al* (1985) from 70 to 400 K, Stewart and Collocott (1989) from 2 to 30 K and Collocott *et al* (1988) from 0.3 to 6 K. These data on heat capacity C_p were all obtained on the same single-crystal specimen as used in this work, and showed that transitions at $T_N = 132$ K, $T_R = 17.3$ K are second order while that at $T_c = 19.5$ K is first order with a latent heat $L = 2.7 \pm 0.3$ J mol $^{-1}$. Dilatometric measurements (Tindall *et al* 1977) had suggested a first-order discontinuity in length at 132 K as well as at T_c . The earlier measurements of length change with strain gauges (Rhyne *et al* 1967) showed the highly anisotropic character of the expansion (and contraction) with bumps near 132 and 20 K. Ultrasonic measurement have shown additional anomalies, particularly in the shear stiffness c_{44} at temperatures near 25 and 96 K (Bates *et al* 1988, Palmer and Lee 1972).

Here we report measurements of thermal expansion from 2 to 150 K for the same crystal used by Jayasuriya and co-workers with the purposes of:

- (i) checking the nature of the transition near $T_N = 132$ K and at T_c and T_R (note that dilatometry can be a clearer indicator of first-order character than heat capacity);
- (ii) determining the anisotropy of expansion, and the volume coefficient β ; and

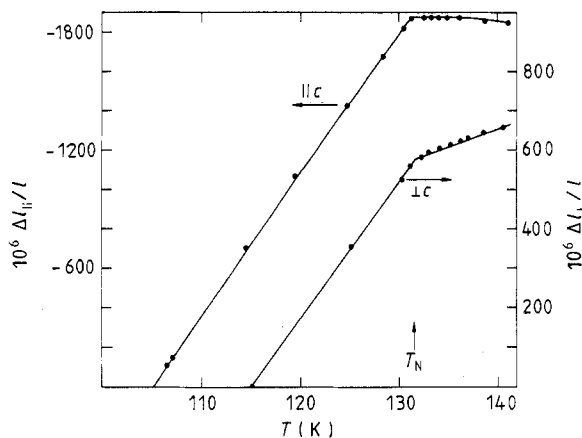


Figure 1. Length changes $\Delta l/l$ (with arbitrary zero) near to $T_N = 132$ K.

(iii) looking for a hyperfine term analogous to that in the heat capacity C_P (see, e.g., Collocott *et al* 1988).

Such a hyperfine term has been suggested by Hirschkoﬀ and Wolcott (1965) and observed in Pr by Ott (1975). We confirm that the transition at T_N is continuous, i.e. not first order, and see no hyperfine bump in α or β .

2. Measurements

The linear thermal expansions were determined in a three-terminal copper capacitance cell (White and Collins 1972) with sensitivity of $\sim 10^{-9}$ cm. The sample is discussed in detail by Jayasuriya *et al* (1985)—see also Jayasuriya (1984). It was prepared at the Ames Laboratory of Iowa State University, with purity 99.9 at.%, in the form of a ‘rod’ approximately 30 mm long \times 14 mm \times 7 mm with maximum length in the direction normal to the c axis. We spark cut, ground and lapped the end faces to produce a ‘rod’ 25 mm long for which length changes Δl_{\perp} and expansivity α_{\perp} were determined from 2 to 145 K and 273 to 293 K. Later the ‘rod’ was spark cut to produce two pieces which when mounted together gave a sample length of 19 mm in the c direction so that Δl_{\parallel} and α_{\parallel} could be measured. Temperatures were measured below 13.8 K with a germanium thermometer and above 13.8 K with a platinum thermometer each calibrated in the laboratory and believed accurate to within a few mK.

3. Results

The length changes (see figures 1–3) show clearly that there is discontinuity in both c - and a -directions at 19.5 K but *not* at 132 K.

The values of the linear coefficients α_{\perp} and α_{\parallel} are shown in figures 4 and 5 while smoothed values are given in table 1 together with the volume coefficient $\beta = 2\alpha_{\perp} + \alpha_{\parallel}$. The coefficients are rather inaccurate in the vicinity of the transitions because of the relatively large changes in $l(T)$ over the temperature intervals, $\Delta T > 0.2$ K, that we used.

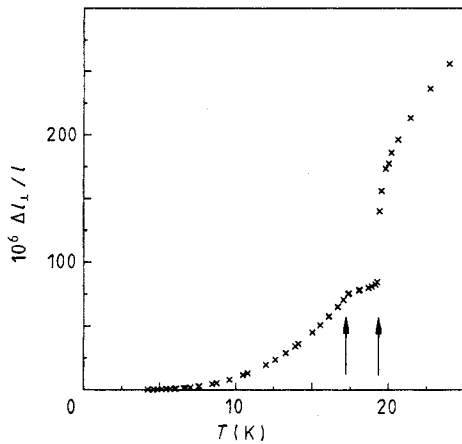


Figure 2. Length changes $\Delta L_{\perp}/l$ below 25 K. Arrows indicate T_R ($=17.3$ K) and T_c ($=19.5$ K).

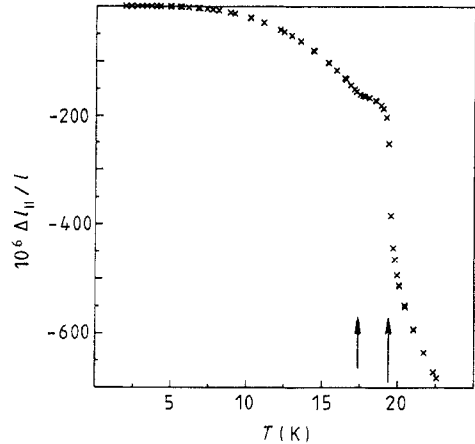


Figure 3. Length changes $4\Delta L_{\parallel}/l$ below 25 K.

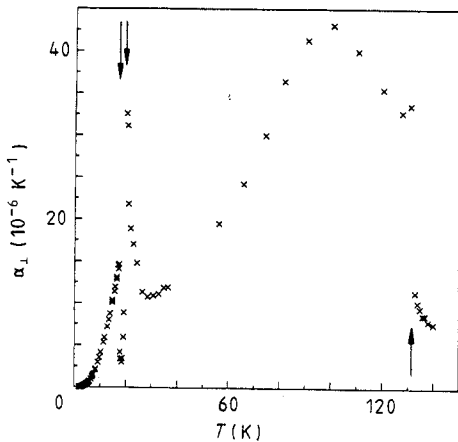


Figure 4. The linear coefficient of thermal expansion $\alpha_{\perp}(T)$.

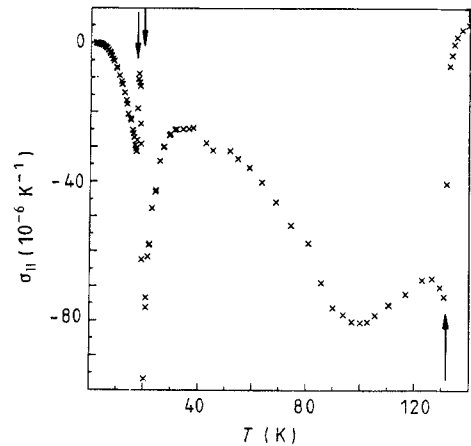


Figure 5. The linear coefficient of thermal expansion $\alpha_{\parallel}(T)$.

In table 1 we also give values of heat capacity at constant pressure, C_p , taken from Collocott *et al* (1988) below 6 K, Stewart and Collocott (1989) from 6 to 30 K, Gerstein *et al* (1957) from 35 to 80 K and Jayasuriya *et al* (1985) above 80 K. In calculating the Grüneisen parameter $\gamma = \beta V B_S / C_p$, we used values of adiabatic bulk modulus $B_S = 41$ GPa at low temperatures and 40 GPa at 283 K (from Palmer and Lee 1972). The molar volume $V \approx 18.5$ ml.

4. Discussion

The results follow the pattern first reported by Rhyne *et al* (1967) and later by Tindall *et al* (1977) (see also Steinitz *et al* 1987) except that the length changes near 132 K show no evidence of the first-order character suggested by Tindall *et al* (1977). Possibly their effect arose because they did not correct for expansion of the beryllium-copper cell.

Table 1. Present thermal data for holmium (data sources for C_p are given in the text).

T (K)	α_{\parallel} (10^{-6} K^{-1})	α_{\perp} (10^{-6} K^{-1})	β (10^{-6} K^{-1})	C_p ($\text{J mol}^{-1} \text{ K}^{-1}$)	γ
2.5	-0.08	0.06	0.04	0.648	<0.1
3	-0.17	0.10	0.03	0.485	<0.1
4	-0.43	0.24	0.05	0.347	<0.1
5	-0.88	0.475	0.07	0.370	<0.1
6	-1.59	0.82	0.05	0.531	<0.1
7	-2.67	1.37	0.07	0.838	<0.1
8	-4.13	2.09	0.05	1.250	<0.1
9	-5.91	2.95	-0.01	1.78	<0.1
10	-7.93	3.94	-0.05	2.40	<0.1
12	-12.9	6.29	-0.3	3.82	<0.1
14	-19.8	9.22	-1.4	5.43	-0.2
16	-26.7	12.2	-2.3	7.16	-0.2
17	-29	14.2	-0.6	8.10	-0.05
$T_R = 17.3 \text{ K}$					
18	-10	3.5	-3	8.16	-0.3
19	≈ -100	≈ 10	≈ -80	8.82	≈ -8
$T_c = 19.5 \text{ K}$					
19.5	≈ -500	≈ 200	≈ -100	≈ 100	—
20	-140	40	-60	10.6	-4
22	-58	18	-22	11.4	-1.5
24	-43	14	-15	12.1	-1.0
26	-33.5	12	-9.5	13.2	-0.5
28	-28	11	-6	14.3	-0.3
30	-26	11	-4	15.4	-0.2
35	-25	12	-1	18.0	-0.05
50	-30	17	4	24.5	0.1
55	-33	19	5	26.3	0.15
60	-37	21.5	6	28.0	0.15
70	-47	27	7	31.0	0.2
80	-60	35	10	34.0	0.2
90	-75	41	7	37.0	0.15
100	-80	43	6	39.7	0.1
110	-75	40	5	41.0	0.1
120	-70	35.5	1	42	<0.1
125	-68	33.5	-1	43	<0.1
130	-71	33.5	-4	45	0.1
$T_N = 132 \text{ K}$					
135	0	9.5	19	28	0.51
140	5	7.5	20	27	0.56
283	16.8	3.7	24.2	27.5	0.65

The calorimetry by Jayasuriya (1984) and Jayasuriya *et al* (1985) shows a second-order transition at this temperature. The present results confirm a first-order transition near 19.5 K, and a second-order change near 17.3 K—both in confirmation of the calorimetric measurements of Stewart and Collocott. We do not see any irregularities near 96 K or 25 K despite the fact that anomalies are seen in the shear stiffness c_{44} (Bates *et al* 1988) at these temperatures.

From the length discontinuities observed near 19.5 K, we estimate $\Delta c/c = -(245 \pm 15) \times 10^{-6}$, $\Delta a/a = (85 \pm 5) \times 10^{-6}$ whence $\Delta V/V = -(75 \pm 25) \times 10^{-6}$.

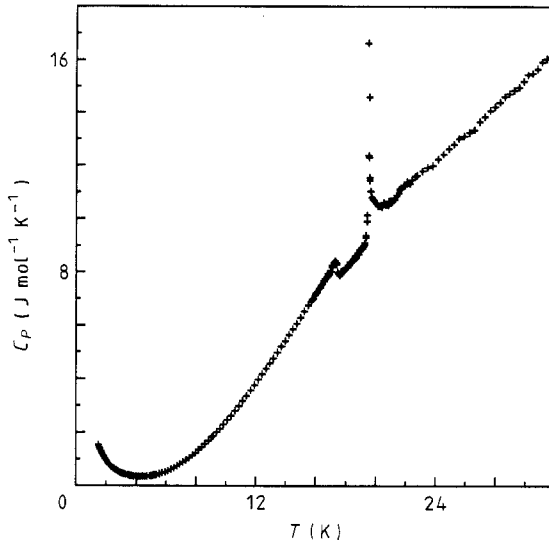


Figure 6. The heat capacity, C_p , from 2 to 32 K (from Stewart and Collocott 1989).

Using a latent heat of 2.7 J mol^{-1} (Stewart and Collocott 1989) we obtain via the Clausius–Clapeyron relation that $dT_c/dP = -10 \text{ K GPa}^{-1}$ (or -1.0 K bar^{-1}) and $d \ln T_c/d \ln V = 21$.

The nature of the phase transitions and neutron and ultrasonic evidence have been discussed in detail elsewhere (see, e.g., Koehler *et al* 1966, Elliott 1972, Cowley and Bates 1988).

Apart from these features, the other remarkable feature is the anisotropy. We can analyse the present data in terms of the principal Grüneisen parameters, γ_{\parallel} and γ_{\perp} , which are measures of the strain dependence of the entropy, S (see the review by Barron *et al* 1980):

$$\gamma_{\parallel} = (dS/d \ln c)_{a,T}/C_{\eta} \quad \gamma_{\perp} = (dS/d \ln a)_{c,T}/C_{\eta}$$

where C_{η} is the heat capacity measured at constant strain η . We calculate experimental values from

$$\gamma_{\parallel} = (c_{33}\alpha_{\parallel} + 2c_{13}\alpha_{\perp})V/C_p \quad \gamma_{\perp} = [(c_{11} + c_{12})\alpha_{\perp} + c_{13}\alpha_{\parallel}]V/C_p$$

where c_{11} , c_{12} , c_{13} , c_{33} are elastic moduli determined by Palmer and Lee (1972). Typical values obtained from the data in table 1 are: $\gamma_{\parallel} = -3.5$ (10 K), -2.0 (30 K), -2.1 (100 K), $+1.0$ (283 K); and $\gamma_{\perp} = 1.9$ (10 K), 0.75 (30 K), 1.3 (100 K), 0.5 (283 K).

At low temperatures, it is evident from heat capacity data that magnetic forces dominate the entropy and free energy. For example, Stewart and Collocott find in the region of 5–10 K that $C_p \approx 2T^3 \text{ mJ mol}^{-1} \text{ K}^{-1}$ whereas the lattice contribution (from elastic data) should be $\approx 0.3 T^3 \text{ mJ mol}^{-1} \text{ K}^{-1}$. It follows that these strain dependences γ_{\parallel} , γ_{\perp} parallel and normal to the symmetry axis are a good measure of the response of the magnetic interactions to such strains: negative for c -axis strain and positive for strain in the basal plane.

Finally we turn to a negative result of these experiments, namely a non-observance of any nuclear hyperfine term, analogous to that in the heat capacity below 4 K (see, e.g., figure 6). Hirschkoﬀ and Wolcott (1965) first pointed out that if there is a nuclear

moment and the hyperfine field at the nucleus is sensitive to the volume or lattice spacing, then a Schottky 'bump' must occur in the expansion coefficients as well as in the heat capacity. For example, they predicted for cobalt a contribution $\alpha_{\text{nuc}} \approx 0.1 \times 10^{-8}/T^2$, based on the change in the nuclear magnetic resonance frequency under pressure amounting to $d \ln \nu/d \ln V = -1.2$ (or $\gamma_{\text{nuc}} \approx +1.2$). Recently we looked for such a term for polycrystalline cobalt using a capacitance dilatometer mounted in a dilution refrigerator, and concluded that it might exist but was not identified clearly above the vibrational noise. For holmium, if $\gamma_{\text{nuc}} \approx 1$, as Hirschkoﬀ and Wolcott assumed, then a very much larger nuclear contribution should be present, i.e. α_{nuc} should be of the order of $250/T^2 \times 10^{-8} \text{ K}^{-1}$. Ott (1975) measured $\alpha_{\parallel}, \alpha_{\perp}$ for a crystal of Pr and found nuclear contributions below 2 K to be given by $-90/T^2 \times 10^{-8} \text{ K}^{-1}$ (\parallel) and $67/T^2 \times 10^{-8} \text{ K}^{-1}$ (\perp). If there were similar behaviour in holmium, then the linear expansion or contraction should have increased noticeably below 3 or 4 K, which it did not in our experiments. Our conclusion is that the hyperfine splitting in Ho is much less sensitive to volume, i.e. $\gamma_{\text{nuc}} \ll 1$. This is not so surprising if we consider that crystal-field effects (which are highly strain dependent) play a significant role in the hyperfine splitting in light rare earths but not in heavy rare earths.

Acknowledgments

I thank Drs S J Campbell and A M Stewart for the use of their holmium crystal, Dr S J Collocott for his generous help in automating the direct read-out capacitance and thermometer systems and C Andrikidis for much care and hard work in preparing samples.

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