

# Electrical resistance of dysprosium under pressure

B Sundqvist<sup>1</sup> and V K Tolpygo<sup>1,2</sup>

<sup>1</sup> Department of Physics, Umeå University, S-90187 Umeå, Sweden

<sup>2</sup> Honeywell Aerospace, Phoenix, AZ 85034, U.S.A.

E-mail: bertil.sundqvist@physics.umu.se

**Abstract.** The electrical resistance of dysprosium metal has been measured as a function of hydrostatic pressure up to 1.2 GPa at temperatures from 300 K to 700 K, and at atmospheric pressure from 80 to 700 K. Our data at atmospheric pressure and at room temperature agree well with literature data. The total pressure coefficient of resistance at 300 K is found to be  $d\ln R/dp = -2.98 \cdot 10^{-2} \text{ GPa}^{-1}$  and to decrease slightly with increasing temperature. The results are discussed in terms of simple free-electron type models.

## 1. Introduction

Rare earth metals are becoming increasingly important in present-day technology because of their use in displays, magnets and energy-related applications, but many of their physical properties were only measured decades ago and sometimes on samples with questionable purity. Dysprosium is one of the most important of these elements with many commercial applications. It is also one of the best studied of the rare earths and many of its properties have been measured as functions of high pressure.

Most studies of dysprosium under pressure have concentrated on its structural phase diagram and magnetic properties. Early studies of the phase diagram were summarized by Tonkov [1] and Young [2], and recent experiments [3-5] have extended these data to higher pressures. The phase diagram is similar to that of other rare earths [6]; compression results in a structural evolution hcp  $\rightarrow$  hexagonal (Sm-type)  $\rightarrow$  dhcp, but above 40 GPa there is some disagreement about the structures. Near the melting point a bcc structure is also observed. Hysteresis effects are strong and many samples are reported to contain mixed phases over wide ranges of pressure at room temperature, and compression anomalies have recently been reported in both the hcp and Sm-type phases near 2 GPa [7]. Like other rare earths, dysprosium also has a rich magnetic phase diagram [1,8]. It is a ferromagnet below about 85 K, where it transforms into an anti-ferromagnetic phase which persists until the transformation into a paramagnetic state near 178 K. The transition temperatures seem to depend only weakly on pressure.

Dysprosium has a very high electrical resistivity  $\rho$  due to strong spin scattering. At atmospheric pressure the resistivity has been relatively well studied [9], but very few data have been reported for the resistivity of dysprosium under pressure. Several groups have measured the resistance  $R$  to map magnetic and structural transitions but numerical data are rarely given. Also, most studies were carried out in anvil devices using soft solid pressure media. While this is completely acceptable for observing phase transitions, accurate data for the electrical resistivity can only be obtained using a fluid medium to eliminate sample deformation. We therefore here present data for the electrical resistance of dysprosium under hydrostatic pressures up to 1.2 GPa at temperatures from 300 to 700 K.



## 2. Experimental details

Three specimens were studied under high pressure, all cut from a 0.1 mm thick dysprosium foil with a nominal purity of 99.9 percent obtained from Johnson Matthey GmbH (Alfa Products). A certificate of analysis delivered with the foil stated that no rare earth impurities had been detected and that the main impurities were 100 ppm iron and 50 ppm silicon. However, because the analysis was carried out on the raw sample it is reasonable to assume that further iron impurities may have been added during the rolling of the metal into a foil. The samples had widths of 1.08 to 1.38 mm and effective lengths of 6.8 to 7.6 mm, and the initial room-temperature resistances were in the range 65 to 80 m $\Omega$ .

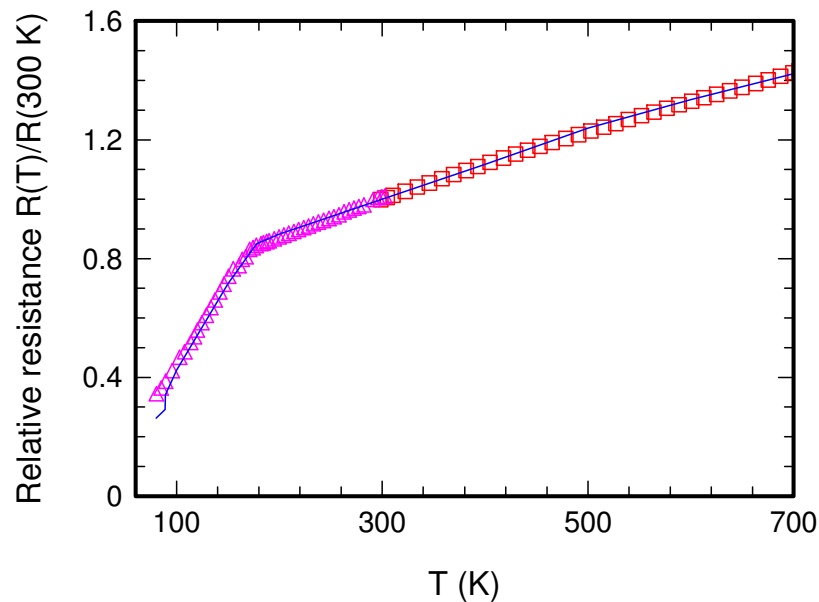
The high pressure measurements were carried out in a piston-cylinder device with an internal diameter of 45 mm. The sample was provided with four connecting wires and inserted into an Al<sub>2</sub>O<sub>3</sub>/Pyrex oven very similar to that used by Sundqvist [10]. The temperature in the oven was measured using a type K thermocouple. We used Dow Corning DC200™ silicone oil, poly (dimethyl siloxane) with a viscosity of 100 mm<sup>2</sup> s<sup>-1</sup> (cSt), as hydrostatic pressure medium in order to be able to study the resistance to well above room temperature. In our experience this silicone does not begin to pyrolyse until the temperature exceeds 700 K, and in this work we have occasionally run the oven up to 745 K for short periods without problems. However, the drawback is that the silicone solidifies at pressures close to 1 GPa at room temperature [11], making the pressure range available rather limited. With metal samples in the shape of thin foils or thin wires solidification of the medium gives rise to significant anomalies such as step changes in the resistance or its temperature and pressure derivatives or hysteresis phenomena. The pressure in the cell was measured using a self-supporting Manganin pressure gage [12] made from wire calibrated against the melting line of mercury.

The resistances of two samples were also measured in a simple cryogenic device down to 80 K at atmospheric pressure (without a pressure medium) to check the agreement with literature data.

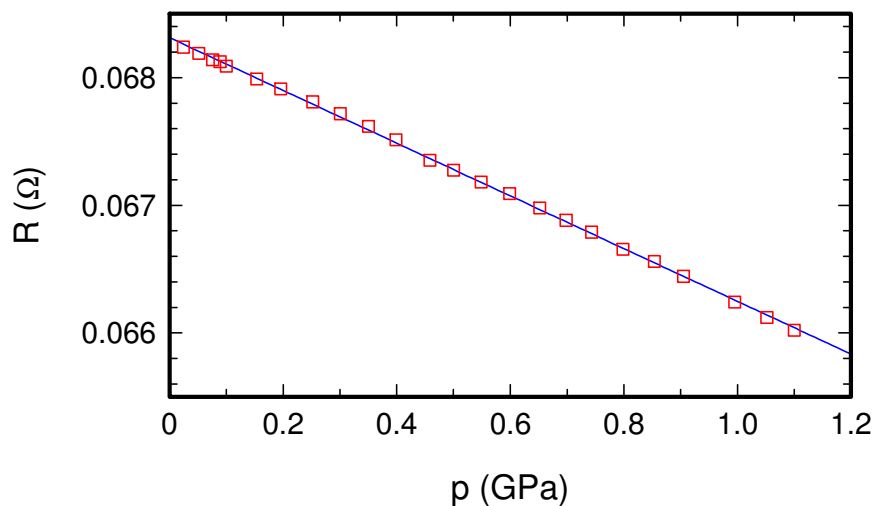
## 3. Experimental results and discussion

Our data for the resistance of dysprosium from 80 K to 700 K at atmospheric pressure are shown by the symbols in figure 1. These data were measured on two samples in different experimental set-ups, a simple cryogenic cell below 300 K and the high pressure cell at and above 293 K. Data obtained for other samples were in excellent agreement with those shown. For comparison, we show as a solid curve data from references [13] and [14]. The transition between the antiferro- and paramagnetic states near 175 K gives rise to an abrupt change in the slope of the resistance data versus temperature. In single crystals a peak is observed in the c-axis resistivity [13]. The lack of a peak in our data probably shows that our foil specimens have been oriented during rolling such that the crystallographic basal plane is preferentially parallel to the plane of the foil. The low temperature data plotted as a line in the figure thus corresponds to the (extrapolated) "in-plane" data given by Hall *et al.* [13]. The agreement between our results and the data in references [13] and [14] is excellent, except that we see only a small change in slope rather than a step change in resistance at the ferromagnetic to antiferromagnetic transition near 88 K. However, it is possible that we did not reach a sufficiently low temperature to complete this transformation which is reported to show some hysteresis. Due to the unfavourable geometry of our specimens it was not possible to calculate the magnitude of the resistivity with good accuracy but the values obtained were of the correct order of magnitude, although somewhat high.

The measured pressure dependence of the resistance of one specimen at 300 K is shown in figure 2. The pressure was changed in steps and at each measurement point we waited until the temperature in the oven was stable and sufficiently close to the desired temperature. The data shown in the figure were measured at (300.0  $\pm$  0.1) K, and most data measured under such strict isothermal conditions showed a similar scatter, although non-linearities or small step changes were noted in some pressure runs. At 300 K measurements were carried out on all three specimens and the resistance was found to be linear in pressure to within the experimental accuracy. The results from one pressure cycle showed a large scatter and non-linearity and a small pressure coefficient, but repeating the experiment gave data in excellent agreement with data for the other samples. The weighted average pressure coefficient at 300 K was found to be  $d\ln R/dp = -2.98 \cdot 10^{-2} \text{ GPa}^{-1}$ .



**Figure 1.** Relative resistance of dysprosium as a function of temperature  $T$  at atmospheric pressure. Data were measured in two separate experiments (symbols) on different samples in different regions of temperature. The full curve shows data from references [13] ( $T < 300$  K) and [14] ( $T > 300$  K).



**Figure 2.** Resistance of dysprosium as a function of pressure for one sample at 300 K.

Most earlier measurements have been carried out using solid pressure media, in which case it is not possible to separate the effects of sample distortion and pressure on the resistance. We are aware of only one single set of resistance data measured under hydrostatic compression: Bridgman [16] measured the resistance of dysprosium at room temperature up to a nominal pressure of  $30 \cdot 10^3 \text{ kg cm}^{-2}$  and found that the resistance was linear in pressure with a pressure coefficient  $\text{dln}R/\text{dp} = -2.40 \cdot 10^{-2} \text{ GPa}^{-1}$  (recalculated in SI units), in reasonable agreement with our result. No correction has been applied for differences in the pressure scales used. Similar values for the pressure coefficient, between  $-1.5$  and  $-3.5 \cdot 10^{-2}$ , can be deduced from measurements in solid media [8,17-19] although the scatter in

the data is usually quite large. The transport properties of dysprosium have also been measured under pressure at temperatures well below room temperature, but in this range there is little numerical agreement between results from different studies [8,17,19].

We measured the pressure dependence of the resistance of two of the samples also at 500 and 700 K. At 500 K we found  $d\ln R/dp = -2.81 \cdot 10^{-2} \text{ GPa}^{-1}$ , while at 700 K one sample gave the very small coefficient  $-2.2 \cdot 10^{-2}$  and the other  $d\ln R/dp = -2.64 \cdot 10^{-2} \text{ GPa}^{-1}$ . In addition to these isothermal cycles we carried out a very large number of isobaric temperature runs, hoping to obtain a continuous record of the pressure dependence between 300 and 700 K, but in most measurements repeatable and reversible anomalies were observed in the temperature dependence. These anomalies were tentatively traced to thermoelectric effects due to temperature gradients inside the oven. Because the accuracy of the data obtained was inferior to that in the isothermal runs we choose to report results only from the latter.

Before a comparison with theory we convert the measured pressure coefficients of resistance to resistivity as  $d\ln \rho/dp = d\ln R/dp - \kappa/3$ , where  $\kappa = 1/B_0 = -d\ln V/dp$  is the isothermal compressibility and  $B_0$  the isothermal bulk modulus. For dysprosium, reported values for  $B_0$  vary between 25 [7] and 40 GPa [16,20]; using the intermediate value 36.3 GPa given in two recent studies [3,4] we find  $d\ln \rho/dp = -3.90 \cdot 10^{-2}$ ,  $-3.73 \cdot 10^{-2}$  and  $-3.56 \cdot 10^{-2} \text{ GPa}^{-1}$ , respectively, at 300, 500 and 700 K. (We have here neglected any temperature dependence in  $B_0$ .)

Assuming the approximate validity of Matthiessen's rule, the resistivity of dysprosium should be the sum of components due to electron scattering on impurities and defects,  $\rho_i$ , phonons,  $\rho_{ep}$ , and a large term due to magnetic (spin) scattering,  $\rho_m$ . In the paramagnetic state well above 175 K the latter should be approximately independent of temperature while the electron-phonon resistivity should be linear in temperature, and the pressure dependence of both terms should also be expected to be independent of temperature. If we know the relative magnitudes of the scattering terms, measurements of  $d\ln \rho/dp$  over a wide range in temperature should thus in principle enable us to deduce the approximate pressure dependence of each major term.

Starting from the simplest possible model and assuming that the disorder term is negligible, a crude linear estimate using the measured data for resistance versus temperature shows that near 300 K the magnetic and phonon terms contribute about 60 and 40 percent of the total resistivity, respectively, and that the ratio is almost reversed near 700 K. Fitting a simple linear model to the data for the total pressure coefficient as a function of temperature we find that the approximate individual pressure coefficients are  $d\ln \rho_{ep}/dp = -2.79 \cdot 10^{-2} \text{ GPa}^{-1}$  and  $d\ln \rho_m/dp = -4.65 \cdot 10^{-2} \text{ GPa}^{-1}$ . The small magnitude of the pressure dependence of the electron-phonon term and the larger magnitude of the spin scattering term are surprising; there are, for example, no indications of an increase in magnetic order under pressure.

The analysis is complicated by the fact that both our data in figure 1 and literature data [9] show  $d^2R/dT^2$  to be negative well above 300 K, probably because the resistivity approaches the resistivity saturation region ( $\approx 200 \mu\Omega\text{cm}$ ) where the electron mean free path is close to the interatomic spacing  $a$ . The saturation resistivity should depend only weakly on pressure and it is possible that the decrease observed in  $d\ln \rho/dp$  with increasing temperature actually arises mainly from this effect. Resistivity saturation can often be well described by a parallel resistor model [21] in which the measured resistivity is modeled as a constant resistivity given by the minimum mean free path, in parallel with the normal resistivity due to scattering by phonons, electrons, impurities, disorder, *etc.* To evaluate this effect we have fitted a parallel resistor model to the data of Habermann and Daane [14] with excellent results, yielding a linear term  $\rho_{\text{normal}} = A + BT$  in parallel to a very large  $\rho_p \approx 325 \mu\Omega\text{cm}$ . Assuming a free-electron-like  $\rho_p = (V/N)mv_F/e^2a \propto V^{1/3}$  and thus  $d\ln \rho_p/dp = -\kappa/3$ , and identifying  $\rho_m \equiv A$  and  $\rho_{ep} \equiv BT$  we have used our results for  $d\ln \rho/dp$  as a function of temperature to find alternative values for the pressure coefficients as  $d\ln \rho_m = -4.4 \cdot 10^{-2} \text{ GPa}^{-1}$  and  $d\ln \rho_{ep}/dp = -5.7 \cdot 10^{-2} \text{ GPa}^{-1}$ .

It is obvious that there is no simple way to analyze the resistivity of dysprosium even at atmospheric pressure, and even less so under elevated pressures. The pressure dependence of the spin disorder term seems to be reasonably well defined and similar in magnitude to the compressibility  $\kappa$ ,

but since there is no simple model available for the spin-disorder scattering [21] we cannot easily compare our results with theoretical predictions. The theoretical pressure or volume dependence of  $\rho_{ep}$  in "simple" metals, on the other hand, is easily found from models of the Bloch-Grüneisen type. The dominant feature is the pressure dependence of the Debye temperature, yielding a simple expression for the dimensionless volume dependence,  $d(\ln\rho_{ep})/d(\ln V) = 2\gamma$ , where  $\gamma$  is the Grüneisen parameter. Various corrections can be applied, but "free-electron-like" models still give  $d(\ln\rho_{ep})/d(\ln V) = 2\gamma + \beta$ , where usually  $|\beta| \leq 1$  but may be of either sign [22,23]. Using the unmodified "2 $\gamma$  law" with  $\gamma = 0.87$  from Gschneidner [24] we find a theoretical  $d\rho_{ep}/dp = -2\gamma/B_0 \approx -4.8 \cdot 10^{-2} \text{ GPa}^{-1}$ , while also taking the pressure dependence of the plasma frequency into account ( $\beta = 1$  [22]) results in  $d\rho_{ep}/dp \approx -7.5 \cdot 10^{-2} \text{ GPa}^{-1}$ . Both values are in reasonable agreement with the results found above, but considering the crudeness of the model this agreement is possibly fortuitous. For many transition metals significant corrections must be applied [25] to obtain agreement with experiment and for high-resistivity metals the use of a saturation model is essential [26]. Still, even for the rare earth metal dysprosium the free-electron model predicts a reasonably correct value for the phonon-limited conductivity under pressure.

### Acknowledgements

This work was financially supported by a post-doc fellowship from the Swedish Institute.

### References

- [1] Tonkov E Yu 1992 *High Pressure Phase Transformations* (Philadelphia, PA: Gordon & Breach) vol. 1 p. 341
- [2] Young D A 1991 *Phase Diagrams of the Elements* (Berkeley, CA: Univ. California) p. 208
- [3] Patterson R, Saw C K and Akella J 2004 *J. Appl. Phys.* **95** 5443-6
- [4] Shen Y R, Kumar R S, Cornelius A L and Nicol M F 2007 *Phys. Rev. B* **75** 064109
- [5] Samudrala G K and Vohra Y K 2012 *J. Phys.: Conf. Series* **377** 012111
- [6] Krüger T, Merkau B, Grosshans W A and Holzapfel W B 1992 *High Pressure Res.* **2** 193-236
- [7] Tschauner O, Grubor-Urosevic O, Dera P and Mulcahy S R 2011 *J. Phys. Chem. C* **116** 2090-6
- [8] Souers P C and Jura G 1964 *Science* **145** 575-7
- [9] Dyos G T and Farrell T 1992 *Electrical Resistivity Handbook* (London: Peter Peregrinus) p. 230-1
- [10] Sundqvist B 1988 *Phys. Rev. B* **38** 12283-9
- [11] Sandberg O and Sundqvist B 1982 *J. Appl. Phys.* **53** 8751-5
- [12] Sundqvist B 1987 *J. Phys. E: Sci. Instrum.* **20** 984-6
- [13] Hall P M, Legvold S and Spedding F H 1960 *Phys. Rev.* **117** 971-3
- [14] Habermann C E and Daane A H 1964 *J. Less-Common Metals* **7** 31-6
- [15] Zinov'ev V E, Gel'd L P, Chuprikov G E and Moreva N I 1974 *Fiz. Tverd. Tela* **16** 358-61
- [16] Bridgman P W 1954 *Proc. Am. Acad. Arts Sci.* **83** 3-12
- [17] Stager R A and Drickamer H G 1964 *Phys. Rev.* **133** A830-5
- [18] Stromberg H D and Stephens D R 1964 *J. Phys. Chem. Solids* **25** 1015-22
- [19] Kawai N, Sakakihara M, Morizumi A and Sawaoka A 1967 *J. Phys. Soc. Japan* **23** 475-6
- [20] Grosshans W A and Holzapfel W B 1992 *Phys. Rev. B* **45** 5171-8
- [21] Glasbrenner J K, Belashchenko K D, Kudrnovský J, Drchal V, Khmelevskyi S and Turek I 2012 *Phys. Rev. B* **85** 214405
- [22] Grimvall G 1986 *Thermophysical Properties of Materials* (Amsterdam: North-Holland)
- [23] Lawson A W 1956 *Progress in Metals Physics* vol. 6 eds Chalmers B and King R (London: Pergamon Press) pp. 1-44
- [24] Gschneidner K A, Jr 1964 *Solid State Physics* vol. 16 eds Seitz F and Turnbull D (New York: Academic Press) pp. 275-426
- [25] Sundqvist B, Neve J and Rapp Ö 1985 *Phys. Rev. B* **32** 2200-12
- [26] Sundqvist B 1992 *Phys. Rev. Lett.* **69** 2693-6