High Pressure: Effect on Dysprosium

Abstract. *The electrical resistance of dysprosium was studied in the temperature-pressure range 77° to 200°K and 15 to 120 kb. The variations of the Néel transition with pressure was found to good accuracy, the value of* dT_N/dP *being* -0.62 ± 0.4 *deg/kb. From this result, second-order thermodynamic equations yield values of* -64×10^{-6} $(°C)^{-1}$ *and* 4.0×10^{-14} $cm^2/dyne$ *for the changes in the coefficient of linear expansion and the compressibility, respectively, at the 1-atm Néel point. The Néel transition disappears at 45 to 55 kb, and no magnetic transitions are seen at higher pressures in the temperature range indicated. The other boundaries in the region investigated have been determined but are very uncertain. The cause of the cusp in the isothermal compressions is not clear from the available data. Above the Néel boundary, the pressure dependence of the cusp with respect to temperature,* dP/dT*, is very small and may even be zero. Below the Néel temperature,* dP/dT *is uncertain. From isothermal measurements, the value is −1, while from the isobaric measurements a value of −0.25 is obtained.*

The unfilled $4f$ shell of dysprosium gives rise to its magnetic properties. Below 85°K at 1 atm, dysprosium is ferromagnetic; between 85° and 178.5°K, it is antiferromagnetic; and above 178.5°K it is paramagnetic (*1*). Neutron diffraction (*2*) shows the antiferromagnetic structure to consist of ferromagnetic sheets perpendicular to the *c*-axis of the hexagonal-close-packed structure. The moments of these sheets spiral as one moves along the *c*-axis. The turn angle between one plane and the next is 26.5 degrees at the Néel point and 43.2 degrees at the Curie point.

The Néel transition is second order, as confirmed by the continuity of the lattice parameters at the transition point (*3*). In the paramagnetic state, both lattice parameters, *a* and *c*, decrease as expected with decreasing temperature. Below the Néel point, *a* continues to decrease but *c* increases as a result of the magnetic forces coming into play in the antiferromagnetic state.

The Néel point of dysprosium is easily seen in the resistivity-temperature graph, as shown by the 40-kb isobar in Fig. 1. The Néel point is particularly well marked by the change in the slope of the resistivity-temperature curve at that point along with a small resistivity peak. At one atmosphere, the present technique of temperature resistance measurements reproduces the data of Spedding and co-workers (*1*). Most of the observed resistivity is due to spin-disorder scattering (*4*), which arises from the interaction of the conduction electrons with any disordered spins on lattice sites. This spin disorder increases with temperature until complete randomness occurs in the paramagnetic state. Hence the spin disorder and the observed resistivity level off above the Néel point. The resistivity peak at the Néel point (as well as the rise at the Curie point) is caused by a small additional contribution to the resistivity by the antiferromagnetic state. Single crystal work (*5*) indicates that this antiferromagnetic state contribution to the resistivity is a maximum for current moving along the *c*-axis and vanishes along the *a*-axis. The added resistivity is due to the periodic spin structure along the *c*-axis (*6*).

In the resistivity-pressure curve of dysprosium, Bridgman (*7*) found a shoulder at about 70 kb. A correction of his pressure scale yields a value in the range 52 to 55 kb. Stephens and Stromberg (*8*) obtain a room-temperature value of 52 ± 1 kb. This shoulder may be seen in the isotherms in Fig. 2.

The ferro-antiferromagnetic Curie transition has been examined under pressure by Swenson, and a value of dT_c/dP of −1 deg/kb (*9*) was obtained. The highest pressure attained does not seem to have been higher than a few kilobars.

Spectral analysis of the dysprosium (*10*) showed 0.1 percent Al, 0.1 percent Ca, and 0.04 percent Mg. The aluminum and magnesium were probably present as impurities in the hydrochloric acid that was used to dissolve the dysprosium before it was plated onto the electrodes.

The dysprosium was too hard and brittle to be extruded into a wire. The 3½-mil foil was cut with a razor into strips 1.3 by 0.010 cm in size. Each strip was bent into a loop and then pressed to about 1½ mils thickness. The edges of each loop were pared with a knife until the width was about 8 mils. The loops were then annealed by heating to 800°C in a high vacuum and cooled slowly to room temperature while still under vacuum. The hard oxide film was scraped off to provide adequate electrical contact.

The Bridgman anvils and the mounting of the samples have been described (*11*). The silver chloride discs in the sample were covered with clear acrylate paint to prevent reaction with the dysprosium. The sample was finally assembled in a dry atmosphere to prevent moisture absorbed by the deliquescent dysprosium chloride from accelerating the dysprosium–silver chloride reaction. The sample was sealed at the edges with acrylate paint to maintain dry air near the hoop until compressed.

The temperature-pressure region between 77° and 200°K and between 15 and 120 kb was covered with both isobars and isotherms. The measurement techniques for pressure, temperature, and resistance, as well as pressure calibration, have been discussed (*12*). Room temperature pressure calibration was used at all temperatures. The isobars were taken with heavy copper blocks (*13*). In both heating and cooling, the temperature was changed at a slow rate of about 0.3 deg/min. These measurements were made slowly in order to obtain the resistivity peak at the Néel point, which does not appear if the temperature is changed too quickly. The temperature difference between the thermocouples above and below the sample was 2 degrees or less. At each pressure on a given sample, the heating and cooling measurements gave the same value of the Néel point to within

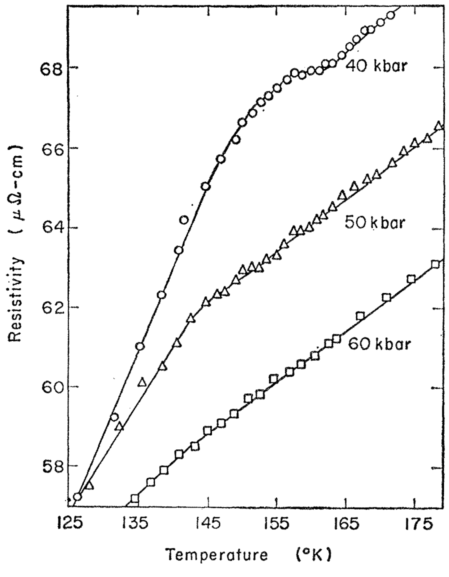

Fig. 1. Resistivity-temperature isobar for dysprosium over a narrow temperature range near the Néel points.

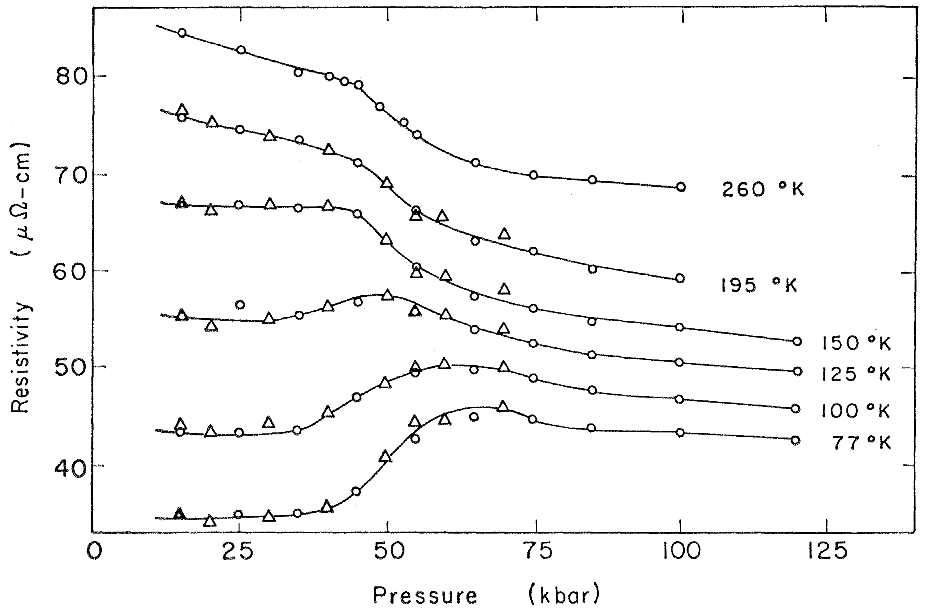

Fig. 2. Resistivity-pressure isotherms for dysprosium derived from the isobaric measurements. Triangles and circles refer to the two isobaric experiments.

a degree. Sets of isobars were taken with different samples over periods of 2 weeks.

Several isotherms were run. Bare anvils were used at room temperature, 195°K, and 77°K with the appropriate baths being used. A single experiment was conducted at 125°K with the copper blocks. These experiments were shorter than the isobar measurements, for the range to 100 kb was covered in only a few hours.

Several of the resistivity-temperature curves for the isobaric experiments are shown in Fig. 1, which covers a narrow temperature range about the Néel points. Three regions of behavior are represented in this figure. From 15 to 45 kb, the resistivity peak at the Néel point, although small, is readily visible. At 50 and 55 kbars, the Néel point is poorly defined. Although the change of slope is still present, the resistivity peak has disappeared. As estimated from measurements below 50 kb, about 6 degrees must be added to the change-of-slope temperature to give the true Néel temperature at the top of the resistivity peak. In the range 60 to 120 kb, the Néel transition has disappeared. No magnetic transitions were seen between 77° and 200°K in this pressure range. Instead, the resistivity is nearly linear with temperature. The phenomenon associated with the resistivity shoulder does not appear in the isobars. The results of the isobaric measurements may be plotted to yield isotherms. These derived isotherms, some of which are shown in Fig. 2, yield phase lines for the phenomenon represented by the resistivity shoulder. In both Figs. 1 and 2, the measured electrical resistance has been converted to resistivity with 92 μohm cm as the room-temperature, 1-atm resistivity of polycrystalline dysprosium (*14*). Bridgman's (*7*) room-temperature resistances at 1 atm and 15 kb were also used.

All the results are shown in the phase diagram in Fig. 3. The Néel point measurements were the best taken in this experiment and the Néel line is well defined. The Néel temperature drops with increasing pressure. The value of dT_N/dP is -0.62 ± 0.04 deg/kb. At pressures above 45 kb, the Néel line begins to disappear as already mentioned. In contrast to the Néel line, the phase lines of the shoulder phenomenon are very poorly defined. The pressures at a given temperature are all higher for the isothermal than for the isobaric experiments. In Fig. 3, phase lines have been drawn through both the isobaric and isothermal points. Above the Néel line, dT/dP is very large according to either type of experiment. The direction of the slope of this line cannot be determined. Below the Néel line, dT/dP varies from -1 to -4 deg/kb depending on whether isobaric or isothermal values are examined. The Néel line seems to disappear in the region where the shoulder phase line occurs.

An attempt was made to equilibrate the dysprosium by pulsing 2 amp of current through for a fraction of a second, thus heating and annealing the sample. One such experiment yielded a room-temperature shoulder pressure of 43 kb. However, this technique is not developed enough to yield reliable values.

The phenomenon associated with the resistivity shoulder seems to be extremely sluggish. At a given temperature, lower pressure values for the shoulder are obtained in the week-long isobaric experiments than in the isothermal measurements covering a few hours. At room temperature, the iso-

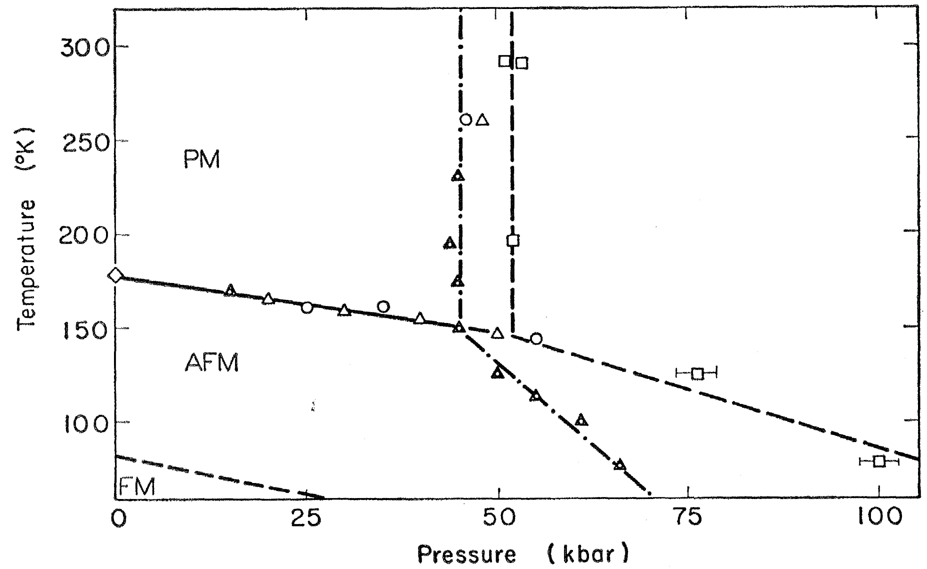

Fig. 3. Temperature-pressure phase diagram for dysprosium. Triangles and circles refer to the isobaric measurements. Squares refer to the isothermal experiments. The diamond is the 1-value (*1*). *FM, AFM,* and *PM* denote the ferro-, antiferro-, and paramagnetic states, respectively.

baric shoulder pressures seem to be fairly reproducible in the region of 46 kb. Similarly, the isothermal pressures cluster about 52 kb, in agreement with Stephens and Stromberg. Probably the lower value is closer to the true equilibrium pressure, since the dysprosium is presumably better equilibrated.

The 15- and 20-kb isobars were carefully measured in the temperature region above 77°K, but the Curie transition was not found. This confirms Swenson's report (*9*) that the Curie temperature decreases with pressure.

Two new properties of dysprosium may now be calculated by means of the Clausius-Clapeyron type equations for second-order transitions (*15*). At the Néel point

$$\frac{dT}{dP}=\frac{TV\,\Delta\alpha}{\Delta C_p}\,, \qquad \frac{dT}{dP}=\frac{\Delta\beta}{\Delta\alpha}$$

where $\Delta\alpha$, $\Delta\beta$, and ΔC_p are the changes in the coefficient of linear expansion, compressibility, and heat capacity at constant pressure, respectively. The values for the 1-atm Néel point are -0.62 deg/kbar and 8.5 cal/deg mole^{-1} (*16*) for dT_N/dP and ΔC_p, respectively. Values of $\Delta\alpha$ and $\Delta\beta$ are calculated to be $-64 \times 10^{-6}\ (°\text{C})^{-1}$ and $4.0 \times 10^{-14}\ \text{cm}^2/\text{dyne}$, respectively. By way of comparison, α is $8.5 \times 10^{-6}\ (°\text{C})^{-1}$ near the Néel point (*17*) and β is $2.44 \times 10^{-12}\ \text{cm}^2/\text{dyne}$ at room temperature (*18*). The same magnetic forces that cause the lattice parameter c to increase below the Néel temperature are probably related to the very large change in the coefficient of linear expansion.

The resistivity-pressure-temperature curves found in this investigation are rather complex. Above about 75 kb, all of the results appear to be normal in that there is a decrease in resistance with an increase in pressure. Below this pressure there are a number of unusual features in the resistivity behavior. Many different hypotheses can be presented to explain the curious behavior that has been observed. However, on the basis of the available data, no conclusions can be drawn that would appear to be reasonably sound to us.

The nature of the change that occurs at about 50 kb on an isothermal compression is also a complex question. This point is discussed in detail by Jamieson in an accompanying paper (*19*). Professor Jamieson has kept us informed of the progress of his x-ray diffraction work as it progressed. The magnetic nature of dysprosium at the higher pressures is unknown. The one conclusion that seems to be inevitable from both of these investigations is that there is a magnetic change above the cusp. There is also an uncertainty concerning the exact value of the pressure at which the transformation occurs, since there is a discrepancy between the values obtained from the isothermal and isobaric work. Fortunately, this discrepancy is only of about 5 kb.

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Neutral Salts: The Generality of Their Effects on the Stability of Macromolecular Conformations

Abstract. *The effects of various neutral salts on the temperature of the thermally-induced denaturation of the globular protein ribonuclease are described and compared with the effects of these salts on helix-coil transition temperatures in other macromolecules. These agents affect the stability of the native form of macromolecules as diverse as ribonuclease, collagen, DNA, and myosin in very similar ways; salts such as KSCN and $CaCl_2$ serve as very potent general structural destabilizers or denaturants, while salts such as $(NH_4)_2SO_4$ and K_2HPO_4 strongly stabilize the native conformation. The effectiveness of the neutral salts as ribonuclease destabilizers is compared with that of urea and the guanidinium salts.*

For many years, intramolecular (primarily peptide) hydrogen bonds were considered to be the main noncovalent source of structural stability in native proteins and nucleic acids. Thus the capacity of denaturing agents, such as urea and guanidinium chloride, to disrupt secondary-tertiary structure has generally been attributed to their effectiveness as competitive hydrogen-bond formers. Recently evidence has been accumulating which suggests that nonpolar interactions (hydrophobic bonds), rather than hydrogen bonds, play the dominant role in the maintenance of the native conformation in aqueous solution (*1*). Such views provide a rational explanation of the denaturing activity of largely nonpolar compounds such as sodium dodecyl sulfate. However, the neutral salts, though generally devoid of either obvious hydrogen bonding or hydrocarbon-solubilization potential, can also markedly perturb secondary-tertiary structure. It is the purpose of this report to demonstrate the remarkable generality of the effects of neutral salts on the stability of macromolecular conformations.

Macroscopically, the striking conformational effects of neutral salts were early recognized in their influence on the shrinkage temperature of collagen fibers (*2*) and the melting temperature of gelatin gels (*3*). In comparative studies with a common cation or anion it was found that the ions could be ranked in order of increasing effectiveness in lowering the