Neutron Diffraction Study of Tb and Ho under High Pressure*

H. UMEBAYASHI,† G. SHIRANE, AND B. C. FRAZER
Brookhaven National Laboratory, Upton, New York
AND
W. B. DANIELS
Princeton University, Princeton, New Jersey

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The pressure dependence of the helical turn angle ω of Tb and Ho single crystals was measured by neutron diffraction up to 6 kbar at temperatures above 80°K. At constant $T-T_N$, the relative changes of ω with pressure $(1/\omega)d\omega/dp$ were slightly temperature-dependent, but representative average values were 20×10^{-3}/kbar for Tb and 1.2×10^{-3}/kbar for Ho. These values were explained satisfactorily by a calculation based on Miwa's theory. The values for the pressure coefficients of the Néel temperature of Tb and Ho, as well as of the ferromagnetic transition temperature of Tb, were also obtained and were in reasonable agreement with the reported values. The spiral temperature range in Tb was found to increase with pressure at the rate of 0.3 ± 0.12°K/kbar.

I. INTRODUCTION

It is well known that rare-earth elements with more than half-filled $4f$ electron shells, Tb to Tm, generally undergo two kinds of magnetic transitions, and that they have sinusoidally modulated arrangements of the magnetic moments between the two transition temperatures.[1] The effect of high pressure on their magnetic properties has been studied rather extensively in recent years.[2–9] Below certain critical pressures ($\gtrsim$25 kbar) where crystallographic transitions take place, the magnetic properties change smoothly as functions of pressure. Both the Néel temperature (T_N) and the ferromagnetic transition temperature (T_f) decrease linearly with an increase of pressure. Here T_N and T_f specify the transition temperatures between the paramagnetic and ferromagnetic states. Reported values of the linear coefficients for Tb and Ho are summarized in Table I together with the present results. In addition to the observation of the T_N and T_f shifts, there are measurements of the pressure effects on the saturation magnetization for ferromagnetic Tb[4] and on the electrical resistivity for Tb and Ho.[7,8]

Since the rare-earth metals have well-localized unpaired electrons in an inner $4f$ shell, a good approximation for their magnetic interaction is considered to be an indirect exchange interaction via conduction electrons. Efforts have been made to interpret the results of previous high-pressure experiments in terms of this interaction.[2,4,9,10]

The present paper reports the results of neutron-diffraction experiments on Tb and Ho single crystals under high pressure. Emphasis is placed on the behavior of the helical periodicity under pressure since it is a quantity uniquely observable in a neutron-diffraction experiment. The results obtained are discussed in the light of a theory by Miwa.[11]

II. EXPERIMENTAL METHOD

Single crystals of Tb and Ho were kindly provided by Professor F. H. Spedding and his colleagues at the Ames Laboratory and Dr. R. J. Gambino at IBM Watson Research Center, respectively. The crystals were shaped into cylindrical rods approximately 1 mm in diam and 10 mm in length. The $[1\bar{1}0]$ direction for Tb and the [110] direction for Ho were aligned parallel with the cylindrical axes. The sample was placed in a pressure cell of maraging steel as shown in Fig. 1. The sealing surface of the cone-shaped plug was coated with indium and the high pressure tubing (0.0625 in. o.d., 0.006 in. i.e.) was silver-soldered into the plug. Hydrostatic pressure was transmitted by He gas and was measured by a precision Bourdon tube gauge up to 2.8 kbar and by a calibrated manganese resistance gauge at higher pressures.

As is well known, a helical magnetic structure is characterized by the appearance of magnetic satellite peaks in a neutron-diffraction experiment, and the periodicity of this structure may be calculated from their spacing. In the present experiment, the $(0,0,2\pm\delta)$ reflections of Ho were observed, but for Tb the $(1,1,\pm\delta)$ reflections were chosen since high resolution

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† Now at Central Laboratory, Tohoku Metal Company, Yokohama, Japan.
[1] W. C. Koehler, J. Appl. Phys. **36**, 1078 (1965).
[2] D. B. McWhan and A. L. Stevens, Phys. Rev. **139**, A682 (1965).
[3] D. B. McWhan and A. L. Stevens, Phys. Rev. **154**, 154 (1967).
[4] D. Bloch and R. Pauthenet, in *Proceedings of the International Conference on Magnetism, Nottingham, 1964* (The Institute of Physics and The Physical Society, London, 1965), p. 255.
[5] L. B. Robinson, S. I. Tan, and K. F. Sterett, Phys. Rev. **141**, 548 (1966).
[6] R. S. Vitt and L. B. Robinson, Bull. Am. Phys. Soc. **12**, 308 (1967).
[7] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **81**, 169 (1952); **82**, 83 (1953).
[8] R. A. Stager and H. G. Drickamer, Phys. Rev. **133**, A830 (1964).
[9] I. G. Austin and P. K. Mishra, Phil. Mag. **15**, 529 (1967).
[10] S. H. Liu, Phys. Rev. **127**, 1889 (1962).
[11] H. Miwa, Proc. Phys. Soc. (London) **85**, 1197 (1965).

TABLE I. Pressure coefficient of T_N and T_f.

Tb(°K/kbar) dT_N/dp	Tb(°K/kbar) dT_f/dp	Ho(°K/kbar) dT_N/dp	Methods	Pressure range(kbar)	Pressure medium	References
−1.07±0.03		−0.48±0.01	Initial permeability	4–71	AgCl	2
−0.82±0.1		−0.45±0.15	Initial permeability	0–6	Petroleum ether or He gas	4
−1.0			Initial permeability	0–25	AgCl	5
−1.05	−1.24		Resistivity	0–14	AgCl	6
−0.76±0.05	−1.06±0.10	−0.33±0.05	Neutron diffraction	0–6	He gas	Present study

is obtained in scanning these peaks by rotating the crystal with a fixed counter position.

III. EXPERIMENTAL RESULTS

In Fig. 2 the integrated intensities of the Tb satellite peaks $(1,1,\pm\delta)$ are plotted as a function of temperature at various pressures. Since a thermal hysteresis of about 1 deg was observed for T_f, all the data shown in the figure were taken on cooling. The values for T_N and T_f were obtained by the linear extrapolation of the curves to zero intensity, as shown in Fig. 2, and are plotted as functions of pressure in Fig. 3. The coefficients of linear shift are -0.76 ± 0.05 deg/kbar for T_N and -1.06 ± 0.10 deg/kbar for T_f. Accordingly, the temperature interval in which the helical structure exists expands slowly at the rate of 0.3 ± 0.12 deg/kbar. This value is to be compared with the value 0.19 deg/kbar obtained by electrical-resistivity measurements.[6]

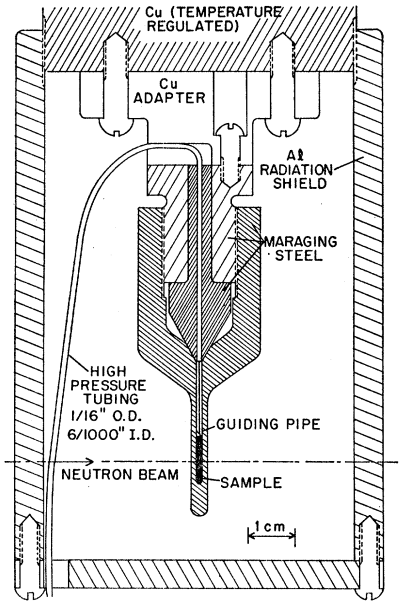

FIG. 1. High-pressure sample holder for neutron-diffraction experiment, designed for pressure up to 10 kbar.

The ratio of the magnetic-structure factor to the nuclear-structure factor for the lower satellite peak $(0,0,2-\delta)$ of Ho is plotted as a function of temperature at various pressures in Fig. 4. The variation of T_N with pressure is plotted in Fig. 3. The observed shift is -0.33 ± 0.05 deg/kbar. At constant T/T_N, any change in the magnetic-structure factor with pressure is less than the experimental error limit (less than 2% in 6 kbar near 80°K).

Our values of the pressure coefficients are very close to those obtained by Bloch and Pauthenet,[4] but are somewhat smaller in absolute magnitude than the values obtained by other investigators (see Table I). The discrepancy may be attributed to the difference in the nature of the pressure-transmitting media (see Table I also).

We turn now to the problem of the effect of pressure on the periodicity of the helical structure. In the case of a simple helical structure propagating in the c direction, as observed in Tb and Ho, the interlayer turn angle of the spins ω can be used to describe the periodicity. Measurement of the angular spacing between the satellite peaks and the lattice parameters at a given pressure permits calculation of ω. The application of pressure changes both parameters. In principle, in-

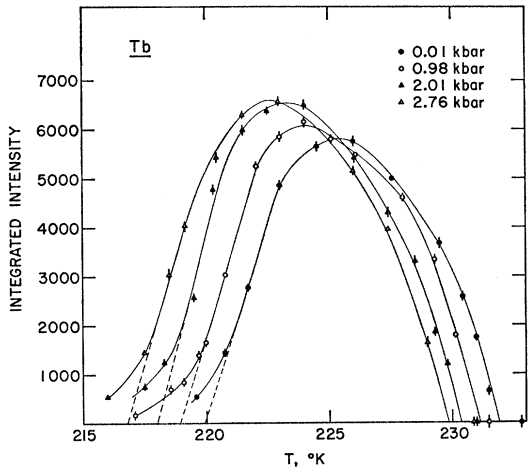

FIG. 2. Temperature dependence for the $(1, 1, \pm\delta)$ reflections of Tb at various applied pressures.

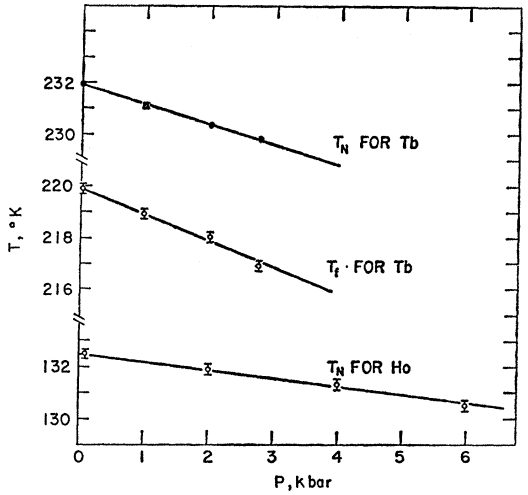

FIG. 3. Pressure dependence of the Néel temperature T_N for Tb and Ho, and of the ferromagnetic transition temperature T_f for Tb.

formation about the lattice contraction under pressure can be obtained from the neutron-diffraction data; however, the accuracy of a lattice constant measurement is much less than that attainable in measuring the satellite spacing. Therefore, the lattice constant changes were estimated by means of the bulk modulus, which was determined from the elastic constants. This correction is found to be important only for the case of Ho. The elastic constants for Ho were herein obtained by interpolation of the reported elastic constants for Dy and Er.[12]

The turn angle ω is plotted as a function of $T-T_N$ at various pressures in Figs. 5 and 6 for Tb and Ho, respectively. The curves for the lowest pressures are in general agreement with the results by Koehler *et al.*,[1] including the *s*-figure temperature dependence of ω for Tb in Fig. 5. Note also that the rise of ω at low

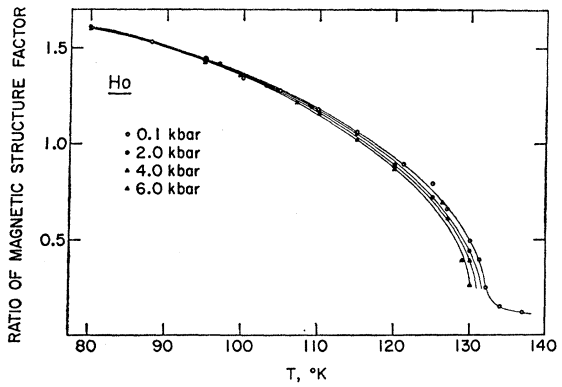

FIG. 4. Temperature dependence of the ratio of the structure factor of $(0, 0, 2-\delta)$ to that of $(0, 0, 2)$ of Ho at various applied pressures.

[12] E. S. Fisher and D. Dever, Trans. Met Soc. AIME **239**, 48 (1967).

temperature in Fig. 5 occurs approximately at the temperature where the satellite intensity decreases (see Fig. 2). The pressure dependence of ω in this temperature range appears complicated because T_f-T_N varies with pressure and the curves are expected to cross one another.

Apart from such complications near the transition temperatures, ω increases with application of pressure. The relative amounts of the change $(1/\omega)d\omega/dp$, at a constant $T-T_N$ in Tb and Ho, are obtained from the graph and listed in Table II for two representative values of $T-T_N$. Note that the value is about one order of magnitude greater in Tb than in Ho.

IV. DISCUSSIONS

Several theoretical treatments have been reported in which the *s-f* exchange model is employed in ex-

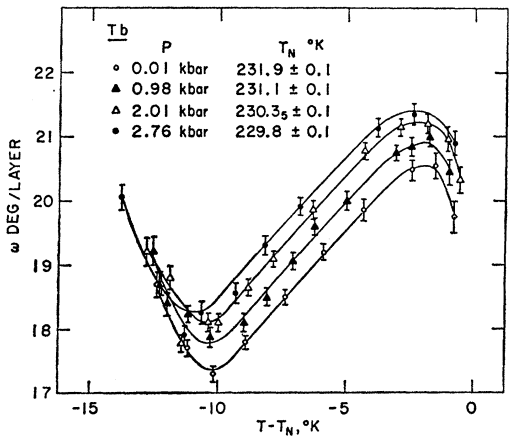

FIG. 5. Turn angle of the spins ω of Tb as a function of $T-T_N$ at various pressures.

plaining the variation of the periodicity of rare-earth helical structures with atomic number and with temperature.[11–15]

It is now generally accepted that the periodicity is determined by the following two factors: the finite mean free path of the conduction electrons, mostly due to the 4*f* spin disorders proposed by de Gennes and Saint James,[14] and the effect of super-zone boundaries for conduction electrons created by the long period modulation of the effective potential proposed by Elliott and Wedgewood.[15] Miwa[11] developed a unified theory in which these two factors were taken into account. According to his theory, the turn angle ω is determined by two parameters ζ and η which characterize the super-zone boundary effect and spin-

[13] K. Yoshida and A. Watabe, Progr. Theoret. Phys. (Kyoto) **28**, 361 (1962).

[14] P. G. DeGennes and D. Saint James, Solid State Commun. **1**, 62 (1963).

[15] R. J. Elliott and F. A. Wedgwood, Proc. Phys. Soc. (London) **84**, 63 (1964).

TABLE II. Change of interlayer turn angle with pressure.

	Tb		Ho	
$T-T_N$	−4.0°K	−9.0°K	−7.0°K	−36.5°K
ω at 1 atm	20.0°	17.7°	50.0°	45.0°
$\omega^{-1}(d\omega/dp)\times10^3$(kbar^{-1})				
Observed	20±2	23±2	1.2±0.2	2.3±0.4
Calculated	19	25	0.6	0.9

disorder effect, respectively. ζ and η are given as follows:

$$\zeta=M^2(V/\epsilon_f)^2, \tag{1}$$

$$\eta=(S^2-M^2)(V/\epsilon_f)^2, \tag{2}$$

where S is the spin quantum number $S=(g-1)J$ (g is Lande's factor), M is the thermal average of S, V is an averaged matrix element of the s–f exchange interactions, and ϵ_f is the Fermi energy. The agreement of this theory with previous experiments was qualitative, but in view of the simplified assumptions adopted, the general approach of the theory would seem to be valid.

In the theory, ω is determined by an equation of the form

$$f(\omega, S, M)=V/\epsilon_f \propto m^{*}v^{2/3}V, \tag{3}$$

where m^* and v are the effective mass of the conduction electrons and the volume of the crystal, respectively. If we discuss the pressure dependence of ω at a fixed reduced temperature T/T_N (actually at a fixed $T-T_N$, but the difference is negligible since the change of T_N with pressure is small), M is approximately constant.

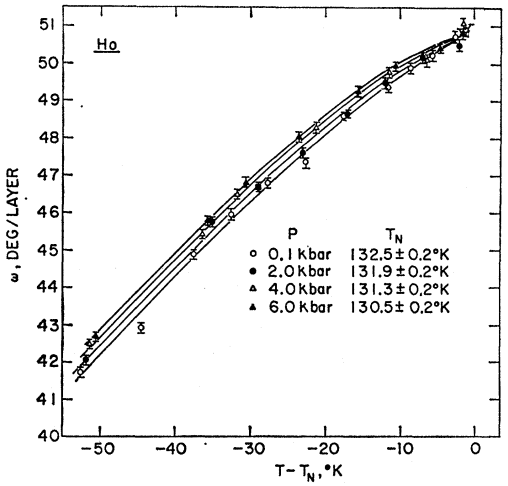

FIG. 6. Turn angle of the spins ω of Ho as a function of $T-T_N$ at various pressures.

In this case the pressure dependence of ω is obtained by

$$\omega^{-1}\frac{\partial\omega}{\partial p}=\frac{-Kf}{\omega f_\omega}\left(\frac{\partial\ln(m^*V)}{\partial\ln v}+\frac{2}{3}\right), \tag{4}$$

where

$$f_\omega=\partial f/\partial\omega.$$

In order to evaluate $(1/\omega)\partial\omega/\partial p$ from Eq. (4), an empirical function was chosen for $f(\omega, S, M)$ which would simulate the experimental equal turn angle contours in the (M^2, S^2-M^2) plane as given by Miwa.[11] The quantity in the parentheses can be evaluated from the pressure dependence of the electric resistivity ρ_m due to spin disorder scattering, as pointed out by Block and Pauthenet.[4]

$$\rho_m^{-1}\frac{d\rho m}{dp}=-K\left(2\frac{\partial\ln(m^*V)}{\partial\ln v}+\frac{5}{3}\right). \tag{5}$$

It is to be noted here that the value for the volume dependence of the exchange integral $\partial\ln V/\partial\ln v$ in Eqs. (4) and (5) should be less by unity than the corresponding value used by Bloch and Pauthenet[4] because of the difference in definition of the exchange parameter.

Using Stager and Drickamer's[8] values for the resistivity change with pressure, and assuming the lattice contribution to the change in resistivity to be negligible,[9] we get the values $(1/\omega)d\omega/dp$ from Eqs. (4) and (5) which are listed in Table II. In view of the crude approximation made, agreement with experimental values is good.

Since there is no great difference between Tb and Ho in the quantity within the parentheses in Eq. (4), the great difference in $(1/\omega)d\omega/dp$ arises from the factor in front. In other words, it may be generally said that in the framework of the present calculation, the longer the wavelength of the periodic modulation, the more sensitive it is to the small change of the conduction band characteristics or the s–f exchange interaction. Evidently this behavior is related to the experimental observation that ω is a steep, decreasing function of the de Gennes factor

$$K=\sum_i c_i(g-1)^2J(J+1)$$

when ω is small,[1] which dependence may be inferred from the experiments on Tb–Y, Tb–Lu, and Tb–Sc[16] alloys as well as for the rare-earth elements. It is also consistent with the fact[1] that when as little as 10% La, which generally tends to diminish ω, is added to Tb, the helical structure becomes unstable and the ferromagnetic structure ($\omega=0$) is realized. The microscopic explanation for this is not clear as yet.

[16] H. R. Child and W. C. Koehler, J. Appl. Phys. **37**, 1353 (1966).

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Heat Capacity of $Mn(NH_4)_2(SO_4)_2\cdot 6H_2O$ near Its Critical Point*

MARTIN RAYL,† O. E. VILCHES,‡ AND J. C. WHEATLEY‡

Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois

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Measurements of the heat capacity of manganese ammonium Tutton salt as close as 4.8×10^{-5} °K to $T_c(\approx0.176$°K) are presented. The measurements were made using both a cerium magnesium nitrate and a chromium potassium alum thermometer. Power- and logarithmic-law fits to the data are possible above $\epsilon\approx10^{-3}$ for a limited range of $\epsilon=(T-T_c)/T_c$. In the power-law fit the heat capacity varies as $\epsilon^{-1/8}$. For smaller ϵ, a pronounced rounding of the heat capacity is observed below and above T_c. In every series of measurements, a T_c could be defined with an accuracy in ϵ better than 3×10^{-5}. A comparison with measurements on other magnetic transitions and a simple hypothesis to explain the "rounding" of the peak are also presented.

I. INTRODUCTION

RECENTLY there has been a great increase[1–7] in theoretical and experimental interest in static phenomena in the vicinity of critical points. The temperature dependence of the heat capacity very near the critical point is one of the quantities of primary interest in this field. The expected temperature dependence can be described by

$$C_+=A_+\epsilon^{-\alpha}+B_+,$$

$$C_-=A_-|\epsilon|^{-\alpha'}+B_-, \qquad (1)$$

where $A_\pm$, $B_\pm$, α, and α' are constants, $\epsilon\equiv(T-T_c)/T_c$, and the subscripts $\pm$ refer to $\epsilon\gtrless0$. In the case of α (or α') equal to zero, Eq. (1) reduces to $C\sim\ln\epsilon$. Excluding size effects, Eqs. (1) are expected to be valid from the transition out to some relatively large ϵ ($\approx10^{-1}$). Previous measurements[8] of the specific heat of manganese ammonium Tutton salt (MATS), $Mn(NH_4)_2(SO_4)_2\cdot 6H_2O$, showed that a λ-type heat-capacity anomaly, a result of a magnetic ordering transition, existed at a temperature of about 0.173°K. Although measurements were carried only to within $\pm10^{-2}$ T_c, their qualitative features indicated that a rapid drop in heat capacity occurred within a temperature interval substantially less than $\pm10^{-2}$ T_c. This stimulated us to believe that perhaps MATS might be an ideal crystal for experimental study, so the present, more precise measurements were undertaken. MATS was also of interest to us since it is a material in which the interaction forces are relatively weak, as indicated by the small value of T_c. Further, the heat capacity is primarily due to magnetic interactions, the lattice contribution being negligible throughout the range of our measurements. Hence the difficulties common to high-temperature experiments in separating magnetic and lattice heat capacities are not present in this one. Moreover, the smaller the lattice heat capacity is with respect to the

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† Present address: R. C. A. Laboratories, David Sarnoff Research Center, Princeton, N.J.

‡ Present address: Department of Physics, University of California at San Diego, La Jolla, Calif. 92037.

[1] M. E. Fisher, in *Lectures in Theoretical Physics* (University of Colorado Press, Boulder, Colo., 1965), Vol. 7c, p. 1.

[2] M. E. Fisher, J. Math. Phys. **5**, 944 (1964).

[3] M. E. Fisher, Natl. Bur. Std. (U.S.) Misc. Publ. **273**, 21 (1966); **273**, 108 (1966).

[4] M. J. Cooper and R. Nathans, J. Appl. Phys. **37**, 1041 (1966).

[5] B. E. Keen, D. P. Landau, and W. P. Wolf, J. Appl. Phys. **38**, 967 (1967).

[6] M. E. Fisher, J. Appl. Phys. **38**, 981 (1967).

[7] L. P. Kadanoff, D. Aspnes, W. Götze, D. Hamblen, R. Hecht, J. Kane, E. A. S. Lewis, V. Palciauskas, M. Rayl, and J. Swift, Rev. Mod. Phys. **39**, 395 (1967).

[8] O. E. Vilches and J. C. Wheatley, Phys. Rev. **148**, 509 (1966).