fitted *versus* the degree of weighting one can evaluate the importance of multiple scattering and its effect on the calculated parameters. Also, one can determine the relative reliability of data from different positions in reciprocal space. Because this method is so simple and powerful it is unquestionably the preferred approach.

It is presumably possible to treat the problem analogously to its treatment for Compton scattering although it is much more complex. A considerable computational effort would also be required (Halonen *et al.*, 1976). Our conclusion is that this approach is so difficult and subject to such uncertainties that it surely should be avoided. It should be pointed out that in certain cases, as for Compton scattering, multiple scattering cannot be eliminated so corrections are necessary; whereas, for diffuse scattering from crystalline solids, the data that are used need not be degraded by this effect.

In summary, I have shown that multiple-scattering processes are important in diffuse-scattering measurements. Data reduction by a multiple-regression analysis can handle the problem most satisfactorily.

References

BORIE, B. S. & SPARKS, C. J. (1964). *Acta Cryst.* **17**, 827–835.
COLE, H., CHAMBERS, F. W. & DUNN, H. M. (1962). *Acta Cryst.* **15**, 138–144.
DUMOND, J. W. M. (1930). *Phys. Rev.* **36**, 1685–1701.
HALONEN, V., EPSTEIN, I. R., TANNER, A. C. & WILLIAMS, B. G. (1976). *Compton Scattering*, edited by B. WILLIAMS. New York: McGraw-Hill.
RENNINGER, M. (1937). *Z. Phys.* **8**, 141–146.
SPARKS, C. J. & EPPERSON, E. P. (1978). Oak Ridge National Laboratory; unpublished work.
WARREN, B. E. & MOZZI, R. L. (1966). *Acta Cryst.* **21**, 459–461.
WILLIAMS, R. O. (1972). *A Computer Program for the Reduction of Diffuse X-ray Data from Solid Solutions.* Report ORNL-4828. Oak Ridge National Laboratory, Tennessee.
WILLIAMS, R. O. (1974). *Metall. Trans.* **5**, 1843–1850.
WILLIAMS, R. O. (1978). *Acta Cryst.* A**34**, 65–73.

Specific heat and compression curves of erbium.

By R. RAMJI RAO and A. RAMANAND, *Physics Department, Indian Institute of Technology, Madras 600036, India*

Abstract

Simple models for the thermal expansion of erbium, and for deducing the magnetic energy from the specific heat, are shown to give an approximate account of the facts. Values are given for the energy of magnetic ordering and the magnetic entropy.

1. Introduction

The heavy rare-earth metal erbium exhibits a rather complex magnetic ordering at low temperatures, which has a pronounced effect on the specific heat. Below a Néel point at 85 K the moments vary sinusoidally along the c axis, and below about 53 K the moments in the basal plane develop a helicoidal ordering. Er is ferromagnetic below 20 K, the helical arrangement of the spins in the basal plane being retained.

We present here calculations for erbium using the nearest-neighbour central-force model proposed by Srinivasan & Ramji Rao (1965), which has earlier been employed to study the lattice dynamics and thermal expansion of erbium (Ramji Rao & Ramanand, 1977). We compute the variation of the lattice parameters with pressure and find good agreement with experiment. We then determine the lattice heat capacity using the central-force model. Subtracting this, and an estimate of the electronic heat capacity, from the specific heat as determined experimentally we obtain a magnetic contribution. This in turn has been used to calculate the total

energy of magnetic ordering, the magnetic contribution to the change in entropy due to ordering and an effective exchange parameter of Er.

2. Effect of hydrostatic pressure on the lattice parameters and volume of erbium

We have followed the method suggested by Thurston (1967) who has derived an expression for the change in the lattice parameter with application of pressure. The usual expression obtained by truncating the power series after the quadratic term is not suitable for extrapolation beyond a few tens of kilobars.

Thurston's extrapolation formula for the principal stretches λ_i ($i = 1, 2, 3$), which is consistent with a linear pressure dependence of the bulk modulus, is

$$\lambda_i = (B/B_0)^{-B_0^2 y_{i0}/(B_0')^2} \exp[(a_i + B_0 y_{i0}/B_0')P]. \quad (2.1)$$

For a uniaxial crystal $\lambda_1 = \lambda_2 = \lambda_\perp$ and $\lambda_3 = \lambda_\parallel$, and equation (2.1) can be written for the two cases:

$$a/a_0 = \lambda_\perp = (B/B_0)^{-B_0^2 y_{\perp 0}/(B_0')^2} \exp[(a_\perp + B_0 y_{\perp 0}/B_0')P],$$

$$c/c_0 = \lambda_\parallel = (B/B_0)^{-B_0^2 y_{\parallel 0}/(B_0')^2} \exp[(a_\parallel + B_0 y_{\parallel 0}/B_0')P]. \quad (2.2)$$

a/a_0 and c/c_0 are the compression ratios of the lattice parameters, B is the bulk modulus at pressure P, B_0 and

B_0' are the bulk modulus and its pressure derivative respectively at zero pressure. In equation (2.2)

$$B_0 = -1/(2a_\perp + a_\parallel); \quad B_0' = B_0^2(2y_{\perp 0} + y_{\parallel 0}),$$

$$y_{\perp 0} = b_\perp - a_\perp^2; \quad y_{\parallel 0} = b_\parallel - a_\parallel^2, \tag{2.3}$$

where

$$a_\perp = -S_1 = -(S_{11} + S_{12} + S_{13}),$$
$$a_\parallel = -S_3 = -(2S_{13} + S_{33}),$$
$$b_\perp = S_1^2 + (S_{11} + S_{12})Q_1 + S_{13}Q_3,$$
$$b_\parallel = S_3^2 + 2S_{13}Q_1 + S_{33}Q_3. \tag{2.4}$$

In equation (2.4)

$$Q_1 = S_1(\beta_{11}' + \beta_{12}') + S_3\beta_{13}'; \quad Q_3 = 2S_1\beta_{13}' + S_3\beta_{33}'. \tag{2.5}$$

Here S_{ij} are the elastic compliance coefficients and the β_{ij}' are the pressure derivatives of the effective elastic coefficients. The theoretical TOE constants obtained using the CF model have been used to calculate the β_{ij}' values (Ramji Rao, 1975; Ramji Rao & Srinivasan, 1968, 1969).

The volume compression ratio is given by

$$V/V_0 = (\lambda_\perp)^2 \lambda_\parallel = (1 + PB_0'/B_0)^{-1/B_0'}. \tag{2.6}$$

We have calculated a/a_0, c/c_0 and V/V_0 for erbium as a function of pressure up to 10^{10} Pa using the parameters of Table 1, and the results are presented in Fig. 1, together with compression data published by Perez Albuerne, Clendenen, Lynch & Drickamer (1966).

There is remarkably good agreement between the calculated values and experiment. Moreover, the calculated values of c/c_0 and a/a_0 are very nearly equal, which means that the axial ratio is very nearly independent of pressure, again as observed.

Table 1. *Parameters used to calculate the compression of* Er

$a_\perp$ $(10^{11}\,Pa)^{-1}$	$a_\parallel$ $(10^{11}\,Pa)^{-1}$	$b_\perp$ $(10^{11}\,Pa)^{-2}$	$b_\parallel$ $(10^{11}\,Pa)^{-2}$	B_0 $(10^{11}\,Pa)$	B_0'
−0·701	−0·798	5·149	7·293	0·4545	3·30
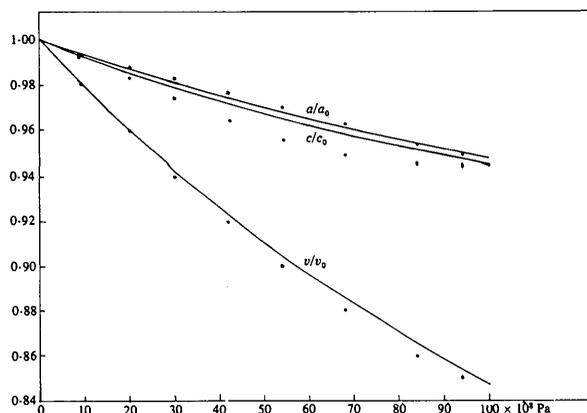
Fig. 1. Pressure dependence of the lattice parameters and volume of erbium. ● experimental values.

3. Calculation of the lattice heat capacity

The frequency distribution function required to calculate the lattice specific heat was obtained by a root-sampling technique. The secular equation for the vibrational frequencies has been solved at 484 points in the irreducible volume of the Brillouin zone. This amounts to using a total of 50 880 frequencies, which are then employed to construct a histogram for $g(\omega)$. In the low-frequency range, where the sampling technique provides too few frequencies to produce a reliable curve, the formula $g(\omega) = C\omega^2$ was used with a value of C obtained from the average of $\sum_{j=1}^3 V_j^{-3} (\theta, \varphi)$ over all directions, where $V_j(\theta, \varphi)$ is the acoustic wave velocity of the jth mode propagating along the direction (θ, φ).

The temperature dependence of the effective Debye temperature obtained using the calculated lattice specific heat is shown in Fig. 2. It is similar to that observed for other rare-earth metals, and the high-temperature limit obtained with this model is in reasonably good agreement with the value of 163 K quoted by Gschneidner (1964).

4. Magnetic contribution to the specific heat

The specific heat of Er has been measured between 3 and 25 K by Lounasmaa & Sundström (1966) and between 15 and 300 K by Skochdopole, Grifel & Spedding (1955). It exhibits a λ-type peak at 85 K and a symmetrical peak at 20 K. Between these two temperatures the specific heat rises rather non-uniformly, with a rounded maximum at 54 K.

In analysing the specific-heat data of the rare-earth metals, it is necessary to consider the lattice contribution C_v^l, the magnetic contribution C_v^m, the electronic contribution C_v^e, and finally the thermodynamic correction δC. Thus

$$C_p = C_v^l + C_v^m + C_v^e + \delta C \tag{4.1}$$

(see, for example, Hofmann, Paskin, Tauer & Weiss, 1956).

The C_p data of Er measured by Skochdopole, Grifel & Spedding (1955) was first converted to C_v using the thermodynamic relation

$$C_v = C_p(1 - AC_pT), \tag{4.2}$$

where

$$A = 9\alpha^2 V/\chi C_p^2. \tag{4.3}$$
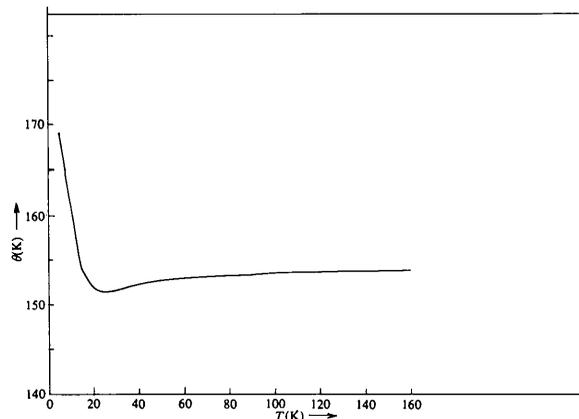
Fig. 2. θ_D vs T for erbium, obtained from the theoretical lattice heat capacity.

The dilation-correction constant A is usually found to be practically independent of temperature; hence the room-temperature value of A quoted by Gschneidner (1964) was used at all temperatures.

The electronic contribution C_v^e was determined as γT using the γ quoted by Lounasmaa & Sundström (1966).

A curve showing the magnetic specific heat for Er derived from (4.1), together with a magnetic entropy curve, is shown in Fig. 3. The energy W of magnetic ordering – the energy required to take the spin system from the magnetically ordered state to the magnetically disordered state – is given by the total area under the magnetic specific-heat curve. The total area under the C_v^m/T vs T curve gives the total entropy gain in the transition from the ordered state to the dis-ordered state. Our values for W and the entropy gain S_{mag} are presented in Table 2.

The value of S_{mag} determined from the present analysis is in fair agreement with the theoretical value, $R \ln(2S + 1)$. However the value of S_{mag} quoted by Rhyne (1972) obtained using a Debye model ($\theta_D = 191$ K) is materially higher than the theoretical value.

To gain some feeling for the significance of W we may crudely make use of a simple Heisenberg model with an exchange integral J between nearest-neighbour spins only. Then the interaction energy $V_{ij} = -2J\mathbf{S}_i.\mathbf{S}_j$, and the energy of magnetic ordering W is given by

$$W = NZS^2|J|, \qquad (4.4)$$

where N is the number of magnetic atoms in the crystal, Z is

the number of nearest magnetic neighbours, and S is the atomic spin. If we also use the elementary formula (Van Vleck, 1941)

$$J/kT_c = 3/2 \, ZS(S + 1), \qquad (4.5)$$

we find that

$$W/NkT_c = 3S/2(S + 1). \qquad (4.6)$$

Equation (4.5) does not, of course, give a particularly satisfacatory way of determining an effective interaction parameter; but, in fact, with $S = 15/2$ and $T_c = 85$ K it gives $J = 0.014$ meV where our W in (4.4) gives 0.013 meV, and so it has the merit of consistency. (4.6) predicts $W/NkT_c = 1.32$, where the value obtained from our analysis is 1.17.

5. Conclusions

Our nearest-neighbours-only central-forces model of erbium is quite successful in explaining the compression data. The agreement is sufficiently good to inspire some confidence in the theoretical third-order elastic constants. The model also yields a magnetic contribution to the total specific heat in reasonable accordance with results deduced from other independent methods.

Table 2. *Results obtained from the analysis of the specific heat of* Er

W (J mol⁻¹)	Magnetic entropy, S_{mag} (J mol⁻¹ K⁻¹)		
	Present analysis	$R \ln (2S + 1)$	From Rhyne (1972)
832	20.9	23.0	25.2
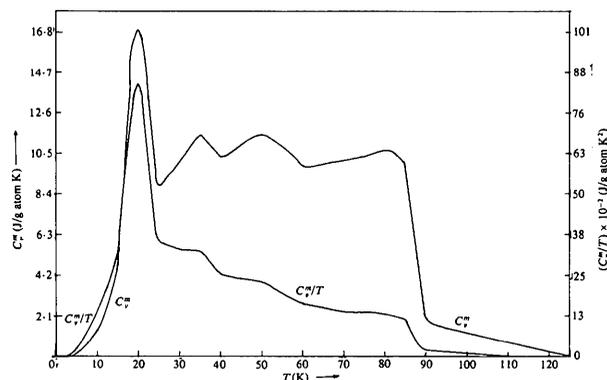
Fig. 3. Magnetic specific heat (C_v^m) and magnetic entropy (C_v^m/T) curves for erbium.

References

Gschneidner, K. A. Jr (1964). *Solid State Phys.* **16**, 275–426.

Hofmann, J. A., Paskin, A., Tauer, K. J. & Weiss, R. J. (1956). *J. Phys. Chem. Solids*, **1**, 45–60.

Lounasmaa, O. V. & Sundström, L. J. (1966). *Phys. Rev.* **150**, 399–412.

Perez Albuerne, E. A., Clendenen, R. L., Lynch, R. W. & Drickamer, H. G. (1966). *Phys. Rev.* **142**, 392–399.

Ramji Rao, R. (1975). *Acta Cryst.* **A31**, 267–268.

Ramji Rao, R. & Ramanand, A. (1977). *Acta Cryst.* **A33**, 146–150.

Ramji Rao, R. & Srinivasan, R. (1968). *Phys. Status Solidi*, **29**, 865–871.

Ramji Rao, R. & Srinivasan, R. (1969). *Phys. Status. Solidi*, **31**, K39–K42.

Rhyne, J. J. (1972). *Magnetic Properties of Rare Earth Metals*, pp. 129–185. New York, London: Plenum.

Skochdopole, R. E., Grifel, M. & Spedding, F. H. (1955). *J. Chem. Phys.* **23**, 2258–2263.

Srinivasan, R. & Ramji Rao, R. (1965). *Inelastic Scattering of Neutrons*, Vol. 1, pp. 325–342. International Atomic Energy Agency, Vienna.

Thurston, R. N. (1967). *J. Acoust. Soc. Am.* **41**, 1093–1111.

Van Vleck, J. H. (1941). *J. Chem. Phys.* **9**, 85–90.