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Effect of correlation and spin-polarisation on the band structure of metallic dysprosium

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Abstract. Energy bands of dysprosium have been calculated considering the effects of correlation and spin-polarisation. The exchange and correlation contributions to the spherically symmetric crystalline potential have been taken in the forms suggested by (i) Kohn and Sham and (ii) Overhauser. The exchange and correlation potential of von Barth and Hedin has been used to study the effect of spin-polarisation on the band structures. The resulting bandwidth, density of states, magnetic moment and spin-splitting have been computed and compared with experimental results. Some discrepancies remain; theoretical calculations done so far agree reasonably among themselves, so accurate experimental data are probably called for.

Keywords. Rare earth metals; dysprosium; energy bands; correlation effect; exchange polarisation; spin-splitting.

1. Introduction

The band structure in dysprosium metal was first calculated by Keeton and Loucks (1968) using the relativistic augmented plane wave (RAPW) method. The crystal potential $V(\mathbf{r})$ was taken in spherically symmetric form and exchange was included in $V(r)$ in the Slater form (Slater 1951). With $4f^{10}6s^2$ atomic configuration the bandwidth was found to be 0·401 Ryd. The density of states histogram showed one peak at Fermi energy ε_F and another at 0·077 Ryd below ε_F. Also it had one minimum at 0·044 Ryd below ε_F. The calculation of the band structures and the conduction electron wavefunctions in the same metal was attempted by Das and Ray (1970, 1971) using the non-relativistic APW method in the context of estimating the conduction electron contribution to crystalline electric field parameters. $V(\mathbf{r})$ was taken in spherically symmetric form and exchange in the Slater form. Since only the three lowest bands were found out, this calculation was incomplete.

Experimental information regarding the band structure in dysprosium is somewhat confusing. From photoemission measurements of Lapeyre (1969) the bandwidth has been found to be $0{\cdot}404 \pm 0{\cdot}015$ Ryd and the density of states curve shows one peak at $0{\cdot}022 \pm 0{\cdot}007$ Ryd below ε_F and one shoulder at $0{\cdot}081 \pm 0{\cdot}007$ Ryd below ε_F. These are thought to correspond to the peaks at ε_F and at 0·077 Ryd below ε_F, respectively, found in the theoretical density of states histogram obtained by Keeton and Loucks. But there is no minimum in the experimental density of states corresponding to the minimum of the theoretical histogram. Photoemission measurements by Mcfeely *et al* (1973) do not, however, show a definite peak near ε_F in contrast to the experimental results of Lapeyre.

From the data on low temperature specific heat measurements, the value of the density of states at the Fermi energy $N(\varepsilon_F)$ has been found to be 54·8 electrons/atom-Ryd by Lounasmaa and Guenther (1962). An analysis of the same data by Morrison and Newsham (1967), however, gives $N(\varepsilon_F) = 103{\cdot}3 \pm 2{\cdot}3$ electrons/atom-Ryd. Such a large difference between these two values and the fact that the electron-phonon enhancement factor is unknown in dysprosium make the comparison of experimental and theoretical values of $N(\varepsilon_F)$ difficult. From the estimate of Pauli paramagnetic susceptibility one gets $N(\varepsilon_F) = 78{\cdot}6$ electrons/atom-Ryd (Arajs and Colvin 1961). Pauli paramagnetism is unaffected by electron-phonon interaction, and it is sometimes advisable to compare the experimental result of the density of states deduced from it with the theoretical result, Kasuya (1966), has, however, introduced an enhancement factor as

$$\eta_d = (1 - \eta_p - \eta_m)^{-1}, \tag{1}$$

with η_p due to phonons being 0·3 and η_m due to magnons being 0·2. Hence the value for the density of states would be 27·4, 51·6 and 62·8 electrons/atom-Ryd, respectively, for the three numbers quoted above.

Like other heavy rare earths, dysprosium has a helical spin structure, the saturation magnetisation is $10{\cdot}3\mu_B$/atom (Rhyne 1972; Lindgard and Danielsen 1975). Considering the effect of zero-point vibration caused by anisotropy the value of conduction electron polarisation M_{ce} has been estimated to be $0{\cdot}41\,\mu_B$. From observations on the infrared absorption spectra on a thin film of dysprosium in both ferromagnetic and antiferromagnetic phases the spin-splitting Δ has been estimated to be 0·44 eV (Cooper and Redington 1965). There exists a relation connecting the conduction electron polarisation and spin-splitting:

$$M_{ce} = \tfrac{1}{4} g \mu_B N(\varepsilon_F) \Delta. \tag{2}$$

Taking $g = 2$ for conduction electrons, we obtain $N(\varepsilon_F) = 25{\cdot}3$ electrons/atom-Ryd.

Spin-polarised band structure calculations in a few other metals have already been done either considering only exchange through Slater form and Kohn-Sham-Gaspar form (Kohn and Sham 1965; Rao *et al* 1975) or considering both exchange and correlation in the form proposed by von Barth and Hedin (VBH) (1972). Callaway and Wang (1974, 1977) have performed such calculations in nickel and iron using different forms of potential, and it may be concluded from their results that, in general, VBH potential gives results in better agreement with the experimental ones.

In the present paper we report the band structure calculations of dysprosium in the non-relativistic APW method with recent accurate potentials including both exchange and correlation effects. This completes the work of Das and Ray. The band structure calculation with the potential which includes the effect of spin polarisation is also reported. The resulting band-width, density of states, magnetic moment and spin-splitting are computed and compared with the experimental results.

2. Construction of the crystal potential

We have used the non-relativistic APW method in our calculation (for details, see Loucks 1967). It will be enough to describe the construction of the crystal potential.

The atomic Coulomb potential in atomic units is given by

$$V_a(r) = \frac{2z}{r} - U_0(r), \tag{3}$$

where z is the nuclear charge and $U_0(r)$ is the electronic contribution. Poisson's equation has been solved with the atomic charge density of Herman and Skillman (1963) to obtain $U_0(r)$. The atomic Coulomb potentials centered about different atomic sites are then superposed to get the Coulombic part of the crystal potential $V^c(r)$. The atomic electron densities are also superposed to get the metallic electron density $\rho(r)$. The superposition has been done by the α-expansion technique of Löwdin (1956).

To get the crystal potential $V(r)$ we have to add to $V^c(r)$ the contribution of exchange and correlation effects. Slater's local exchange approximation is well known, the Kohn-Sham-Gaspar form differing merely by 2/3. The effect of inclusion of the correlation term has been investigated in many metals now. In some cases the effect is only a constant shift of bands with minor modifications in details such as bandwidth or change in sequences at a symmetry point. In other cases a drastic change occurs in the band structure near the Fermi energy and consequently the value of the density of states changes significantly. X-ray emission and photoemission measurements on zinc indicate that the band structure with correlation terms included are more reliable (Nilsson and Lindau 1971). Similarly the experimental results on susceptibility in magnesium are better explained with correlation terms (Ashokamani *et al* 1978).

Several different prescriptions have been proposed for inclusion of exchange and correlation effects. The local exchange-correlation approximation of Kohn and Sham with Wigner's interpolation formula for the correlation energy leads to the following exchange and correlation contribution to $V(r)$ (Rao *et al* 1975).

$$V_{xc,KS}(r) = -\frac{2}{\pi}[3\pi^2\rho(r)]^{1/3} - \frac{0{\cdot}88[\rho(r)]^{1/3}}{0{\cdot}62 + 7{\cdot}8[\rho(r)]^{1/3}} \times \left(1 + \frac{1}{3 + 37{\cdot}72[\rho(r)]^{1/3}}\right). \tag{4}$$

For comparison we also note that the original Slater free-electron exchange approximation gives

$$V_{x,S}(r) = -\frac{3}{\pi}[3\pi^2\rho(r)]^{1/3}. \tag{5}$$

Another simpler expression for the exchange and correlation potential has been proposed by Overhauser (1971):

$$V_{xc,0}(r) = -2{\cdot}07[\rho(r)]^{0{\cdot}3}. \tag{6}$$

For the spin-polarised potential, the suggestion of von Barth and Hedin (1972) has been followed:

$$V^{+}_{xc,BH} = A(\rho)(2x)^{1/3} + B(\rho). \tag{7}$$

The plus sign indicates the spin-up case. A and B are functions of charge density ρ and are given in parametrized form by von Barth and Hedin. x is the fraction of spin-up electrons. For spin-down electrons x should be replaced by $(1-x)$ to get $V^{-}_{xc\cdot BH}$.

The total potential $V(r)$ constructed from these different potentials have been denoted by V_{KS}, V_S, V_0 and V_{BH} respectively.

3. Results

We start with $4f^{10}6s^2$ atomic configuration. The lattice parameters for the dysprosium metal which has hexagonal close-packed structure are $a = 0{\cdot}35903$ nm and $c/a = 1{\cdot}5730$. The radius of the APW sphere has been found to be 3·1582 a.u. and the average potential outside the APW spheres, V_{ave}, has been found to be $-1{\cdot}070$, $-1{\cdot}205$ and $-1{\cdot}077$ Ryd in the cases of V_{KS}, V_S and V_0, respectively. For spin-up electrons the average potential is $-1{\cdot}1103$ Ryd and for spin-down electrons it is $-1{\cdot}0990$ Ryd with V_{BH}.

Figure 1 shows V_{KS} against r. We have found that the deviation for V_0 from V_{KS} is negligible in the whole range of r, but the deviation of V_{KS} from V_S is appreciable. Figure 2 shows the percentage deviation of V_{KS} from V_S. V_S is more negative than V_{KS} in the whole range of r showing that the Slater exchange is overcorrected for the actual correlation effects.

Kohn-Sham potential V_{KS} is not exactly reproduced when we put $x = 1/2$ in the von Barth and Hedin potential. It has been shown by Moruzzi *et al* (1978) that V_{KS} may be reproduced from V_{BH}, if a different parametrized form is used in the latter. We have, however, followed the original parametrized forms of von Barth and Hedin.

Figure 3 shows the resulting bands from the potential V_{KS} along the major symmetry axes of the Brillouin zone. (The bands obtained with the potential V_S are not too different in shape, though shifted in the energy scale and are not presented here.)

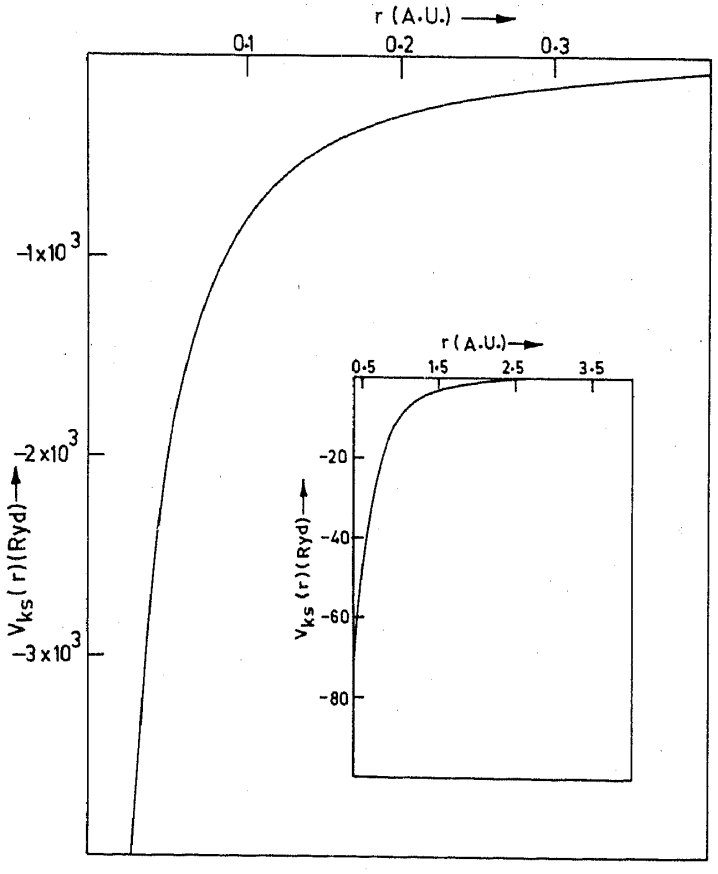

Figure 1. $V_{KS}(r)$ against r.

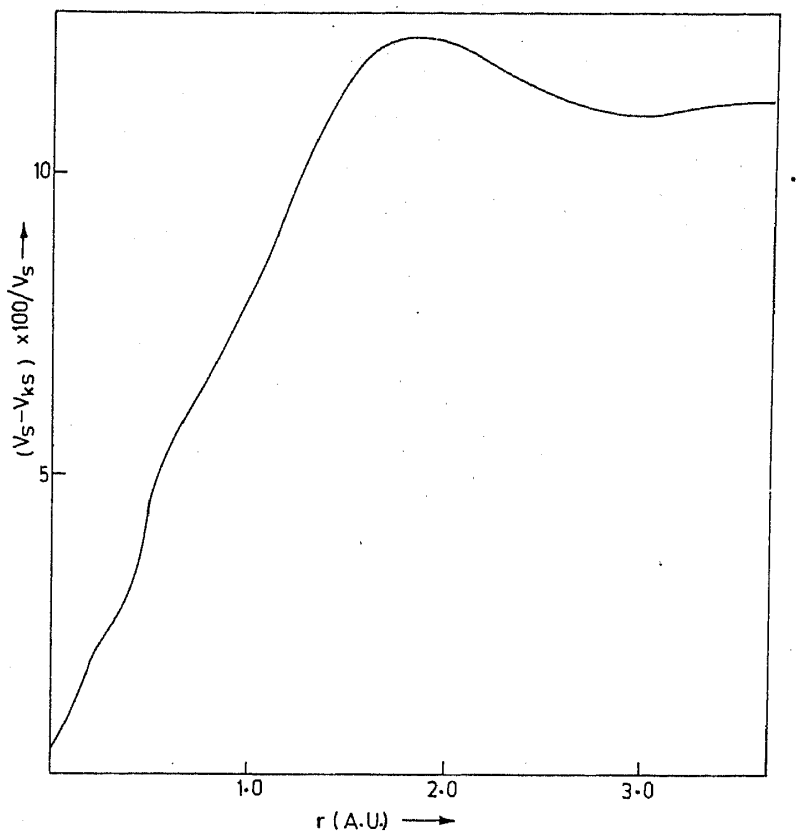

Figure 2. Percentage deviation of V_{KS} from V_S.

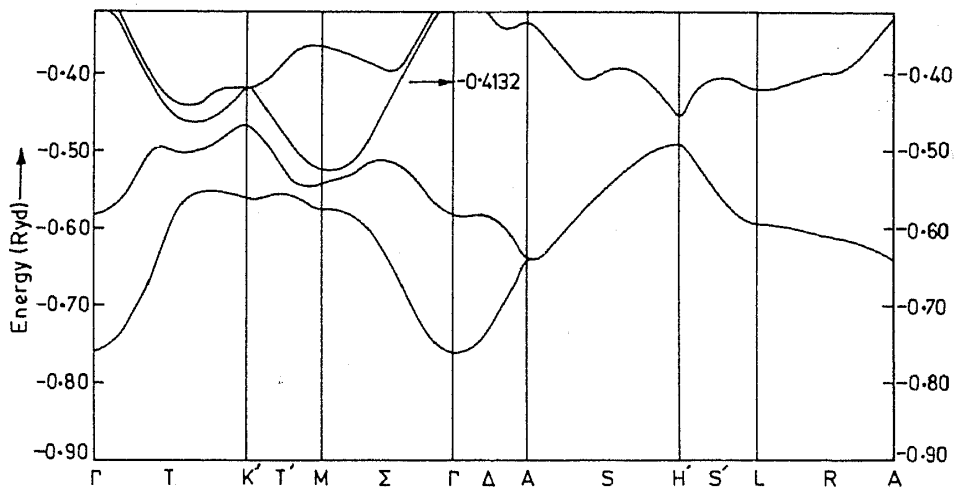

Figure 3. Energy bands with V_{KS}.

Energies have been calculated at 105 general points distributed uniformly within the 1/24th part of the Brillouin zone. These are equivalent to 2100 points in the whole zone. To locate the Fermi level ε_F the states are filled up in the order of increasing energy and the energy corresponding to the highest occupied level gives ε_F. For V_{KS} it is found to be $-0{\cdot}4132$ Ryd.

The density of states histogram has been computed by taking average over five histograms each of bar width $\Delta E = 0{\cdot}025$ Ryd but with different starting points E_n where

$$E_n = E_0 + \tfrac{1}{5}(5-n)\,\Delta E,\ n = 1,2,\ldots,5. \tag{8}$$

E_0 is the energy of the lowest occupied state in the bands. The average histogram has a bar width of 0·005 Ryd. The density of states histogram with V_{KS} is shown in figure 4. Note the two peaks and a minimum in between. The Fermi energy comes at one of the peaks. These features are also true of the density of states with V_S. The value of $N(\varepsilon_F)$ and the bandwidth with V_{KS} and V_S are given in table 1 as also the values of RAPW calculations of Keeton and Loucks (1968). The positions of the peaks and the minimum in each curve are given in table 2.

Figure 5 shows the results of the spin-polarised band structure calculation with V_{BH}. Figures 6 and 7 show the density of states. From the electronic configuration of a

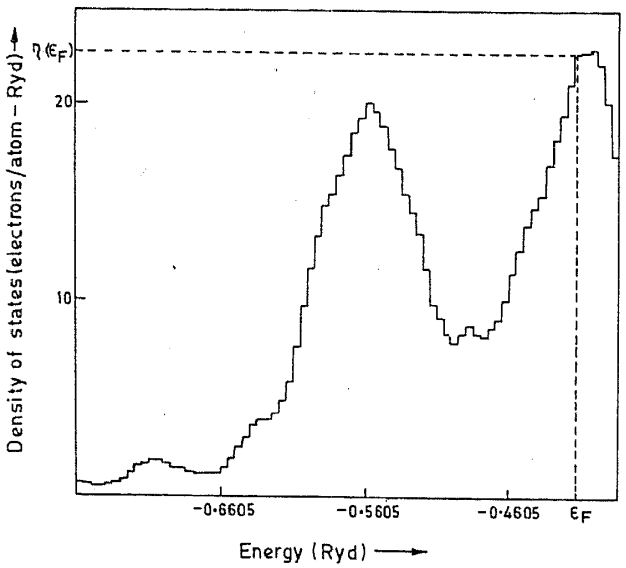

Figure 4. Density of states histogram with V_{KS}.

Table 1. Experimental and theoretical values of different band structure parameters.

	Experimental	RAPW[a]	Present calculation		
			Slater	KS	VBH
ε_F (Ryd)	—	—	−0·6963	−0·4132	−0·4573
Bandwidth (Ryd)	0·404 ± 0·015[b]	0·401	0·315	0·348	0·359
$N(\varepsilon_F)$ (electrons/atom-Ryd)	78·57[c]	24·3	24·7	22·6	22·12
Magnetic moment (μ_B/atom)	0·41[d]	—	—	—	0·28
Spin-splitting (Ryd)	0·032[e]	—	—	—	0·022

[a] Keeton and Loucks (1968); [b] Lapeyre (1969); [c] Arajs and Colvin (1961); [d] Lindgard and Danielsen (1975); [e] Cooper and Redington (1965).

normal dysprosium atom ($1s^2; 2s^2, 2p^6; 3s^2, 3p^6, 3d^{10}; 4s^2, 4p^6, 4d^{10}, 4f^{10}; 5s^2, 5p^6; 6s^2$) the spin polarisation factor x has been taken to be 0·5303. The shape of the bands is very similar to that in figure 3 with V_{KS}, but the spin-up band is shifted relative to the spin-down band. The Fermi energy is −0·4573 Ryd (table 1). The density of states at the Fermi energy $N(\varepsilon_F)$ for the spin-up electrons is 13 and that for the spin-down electrons is 9·12 electrons/atom-Ryd. The total density of states at the Fermi energy is 22·12 electrons/atom-Ryd. The density of states curve shows the usual two-peak structure, with the Fermi energy very close to one of the peaks (table 2). The average spin splitting is 0·022 Ryd compared with the experimental value 0·032 Ryd. The magnetic moment is 0·28 μ_B/atom against the experimental value 0·41 μ_B/atom.

4. Discussion

In this work our principal aim has been to study the effect of correlation and spin-polarisation on the band structures of dysprosium metal. For this we have taken the band structures with exchange in full Slater form as standard and then examined their modifications by these factors. Apart from producing an average shift by 0·27 Ryd the correlation effect causes some minor modifications of the band structures in this case,

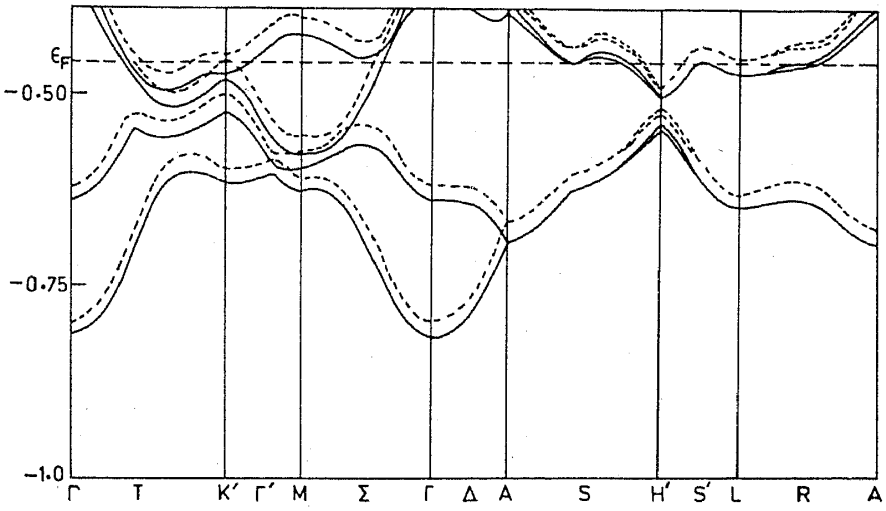

Figure 5. Energy bands with V_{BH}, spin-up bands(——), spin-down bands(------)

Table 2. Position of peaks and minimum in the density of states curve (relative to ε_F). Values are quoted in Ryd unit.

	Experimental[a]	RAPW[a]	Present calculation		
			Slater	KS	VBH
Peak I	−0·022 ± 0·007	0·0	+0·0054	+0·0024	−0·005
Peak II	−0·081 ± 0·007[b]	−0·077	−0·1079	−0·1433	−0·1475
Minimum	No	−0·044	−0·0546	−0·0905	−0·075

[a] Lapeyre 1969; [b] Instead of a peak only a shoulder has been observed.

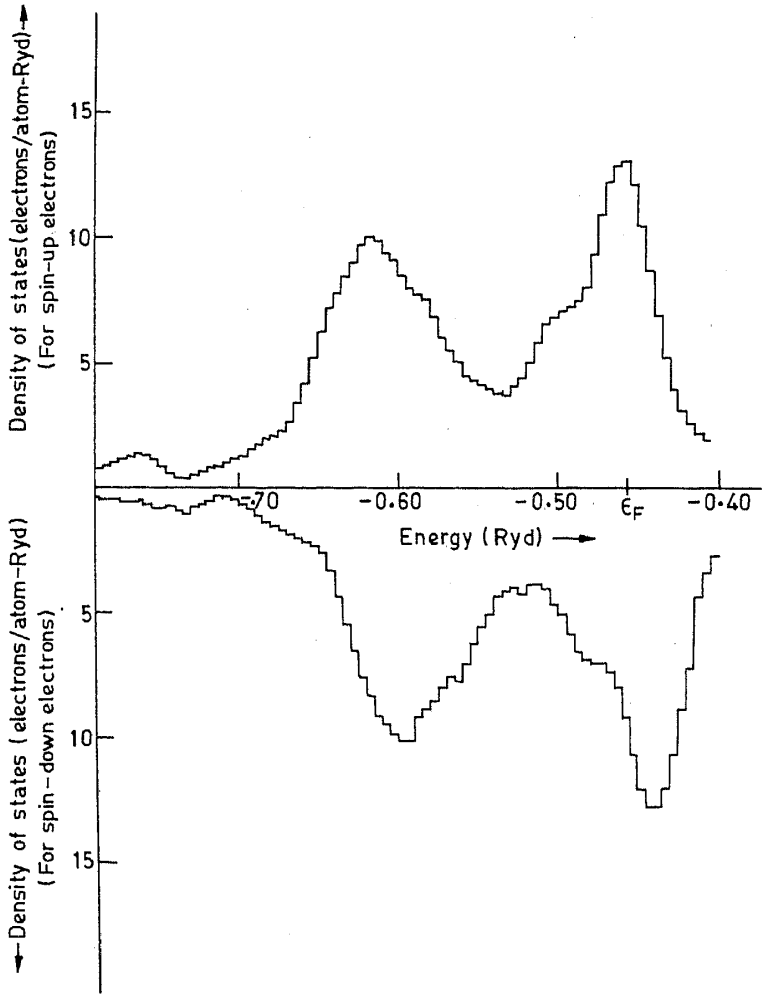

Figure 6. Spin-up and spin-down density of states histogram with V_{BH}.

the value of $N(\varepsilon_F)$ changes by about 7 % and the bandwidth changes by about 8 %. With the inclusion of spin polarisation the bands split but the nature of bands remains the same. The values of $N(\varepsilon_F)$ and the bandwidth change by about 10% and 14% respectively. The average split and the magnetic moment are found to be 0·022 Ryd and 0·28 μ_B/atom respectively. The nature of the density of states histogram as also the positions of peaks and the minimum relative to ε_F are not appreciably altered by the inclusion of correlation or spin-polarisation.

All the theoretical values of density of states at ε_F are far from the experimental value. The value of the bandwidth becomes successively closer to the experimental value with the inclusion of correlation effect and spin-polarisation effect. Theoretical values of the average spin-splitting and the magnetic moment are low and are off by about 30% of the corresponding experimental values. A comparative statement of all the relevant data is given in table 1.

The experimental density of states curve obtained by Lapeyre (1969) shows one peak and a shoulder without a minimum between them in contrast to two peaks and a minimum between them obtained in all the theoretical calculations by us and other authors. This discrepancy also remains unexplained.

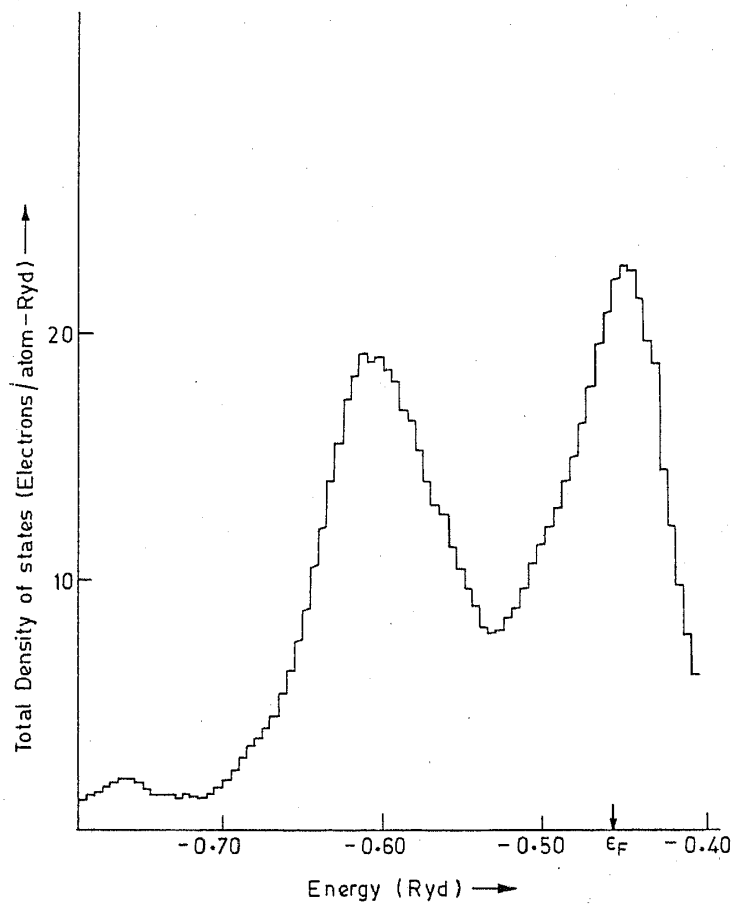

Figure 7. Total density of states histogram with V_{BH}.

5. Conclusion

We have used the non-relativistic APW method in the present calculation and seen that the experimental results, particularly on the density of states, spin-splitting and magnetic moment, are quite off from their theoretical values. One may argue in favour of the relativistic APW method or a self-consistent band structure calculation. But the relativistic APW calculation by Keeton and Loucks (1968) does not show any marked superiority. Their calculated value of density of states at ε_F is rather close to our calculated values and far from the experimental value (table 1). Since the effects of correlation and spin-polarisation have been found to be small in our case, it seems unlikely that these will produce a large change in the relativistic band structures of Keeton and Loucks. No self-consistent calculation of the band structures of metallic dysprosium has yet been reported. But the self-consistent calculation of Belakhovsky and Ray (1975) on the intermetallic compounds DyZn and DyRh shows that V_{ave} and ε_F do not change significantly with successive iterations. So to narrow down the gap between the experimental and theoretical values one has to examine the effects of other factors such as non-spherical potential and electron-phonon interaction.

We note that available experimental data are not very accurate. No Fermi surface studies seem to have been attempted on this metal. It is hoped that the present

calculations would stimulate experimentalists to collect accurate data on Dy and other hcp rare earth metals.

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