

## Contact charge density in metallic dysprosium

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**Abstract.** The contact conduction electron density in metallic dysprosium has been calculated following the APW formalism and taking into account the effects of correlation and spin-polarization. A comparison of this density with that obtained from the Mössbauer isomer shift measurement has been made. An estimate of  $\Delta\langle r^2 \rangle$ , the change in mean square nuclear charge radius between the two levels involved in the  $\gamma$  transition, has been made and compared with those obtained by other workers.

**Keywords.** Dysprosium; Mössbauer isomer shift; contact charge density; energy bands; nuclear charge radius.

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### 1. Introduction

A theoretical estimate of the conduction electron density at a nucleus,  $\rho_c(O)$ , of dysprosium metal, was reported by Das and Ray (1971). They used the non-relativistic APW method and assumed that (i) the potential is in the muffin-tin form, (ii) the exchange part of the potential energy is given by Slater's  $\rho^{1/3}$  form, and (iii) the lowest three conduction bands are full; effects of correlation and spin-polarization were not considered. The calculated value of  $\rho_c(O)$  was found to be  $0.532 \times 10^{26} \text{ cm}^{-3}$ , and it was 3.1 times less than its experimental value as reported by Henning *et al* (1968) from their Mössbauer isomer shift measurements. The difference was attributed to the relativistic effects, though according to Shirley (1964), the relativistic correction factor is 3.99 in atomic case. Henning *et al* also reported  $\rho_c(O)$  for samarium metal. Later Eibschütz *et al* (1972) performed Mössbauer isomer shift measurement in samarium and obtained  $\rho_c(O)$  for samarium metal which is about 60% of the value obtained by Henning *et al*. The observed difference in experimental values of  $\rho_c(O)$  in samarium led the present authors to search for more recent experimental data on  $\rho_c(O)$  in dysprosium also. Pszczoła *et al* (1983, 1984) have reported isomer shift measurement on Dy-Fe compounds and Dy metal, though they have not calculated  $\rho_c(O)$ . In view of the new experimental results on Mössbauer isomer shift and also the assumptions made by Das and Ray in their theoretical estimate of  $\rho_c(O)$ , it is worthwhile to calculate this parameter from more accurate band structure results and compare it with experimental results obtained so far.

In §2 the experimental results have been analyzed to obtain the value of  $\rho_c(O)$ . In §3 we have outlined the necessary theory for the conduction electron density calculation. In §4 the results of our theoretical calculation of  $\rho_c(O)$  have been reported.

In the last section we have obtained an estimate of the product  $S'(Z)\Delta\langle r^2 \rangle$  where  $S'(Z)$  is the relativistic factor of Shirley (1964) and compared it with that obtained by Belakhovsky and Ray (1975).  $\Delta\langle r^2 \rangle$  has also been estimated and compared with results obtained by other workers.

## 2. Analysis of experimental data

In Mössbauer isomer shift experiments the isomer shift is generally given in terms of the relative velocity,  $\delta$ , between the source and the absorber. This is given by the well-known relation (Dunlap and Kalvius 1978),

$$\begin{aligned}\delta &= \frac{2\pi c}{5E_\gamma} Ze^2 \Delta\langle r^2 \rangle \Delta|\psi_0|^2 \\ &= 90.52 \frac{Z}{E_\gamma} \Delta\langle r^2 \rangle \Delta|\psi_0|^2.\end{aligned}\quad (1)$$

Here  $\delta$  is expressed in mm/s,  $E_\gamma$ , the Mössbauer isomer transition energy in keV,  $\Delta\langle r^2 \rangle$ , the difference in nuclear integral between the ground and excited states of the nucleus in  $\text{fm}^2 (= 10^{26} \text{cm}^2)$  and  $\Delta|\psi_0|^2$ , the difference in electronic density at the nucleus for the absorber and the source in  $10^{26} \text{cm}^{-3}$ . The factor  $\Delta\langle r^2 \rangle$  is fixed empirically on the basis of self-consistent field calculations which are strictly valid for free ions. So the applicability of such a value for ions bound in solid is questionable (Kalvius *et al* 1980). Value of  $\Delta\langle r^2 \rangle$  for  $^{161}\text{Dy}$  obtained by different workers are given in table 1. The value  $9.5 \times 10^{-3} \text{fm}^2$  has been estimated by Cashion *et al* (1975) in the light of more recent work using best available ionic compounds. We have calculated  $\Delta|\psi_0|^2$  using all the tabulated values of  $\Delta\langle r^2 \rangle$  and the values of  $\delta$  and  $E_\gamma$  have been taken from the work of Pszczoła *et al* (1984), the value of  $\delta$  given in MHz has been converted to mm/s by using the conversion factor from Shenoy and Dunlap (1978). This  $\Delta|\psi_0|^2$  corresponds to  $\rho_c(\text{O})$ . Because of large differences in the values of  $\Delta\langle r^2 \rangle$  the experimental values of  $\Delta|\psi_0|^2$  are also quite different. Henning *et al* (1968) have avoided the problem regarding the value of  $\Delta\langle r^2 \rangle$  by taking a ratio of two isomer shift measurements. They obtained the value of  $\rho_c(\text{O})$  as  $1.65 \times 10^{26} \text{cm}^{-3}$ . This value is smaller than those obtained from the measurements of Pszczoła *et al* (1983, 1984) except in one case where  $\Delta\langle r^2 \rangle$  value is rather high (table 1).

**Table 1.** Conduction electron density,  $\rho_c(\text{O})$  (in  $10^{26} \text{cm}^{-3}$ ) at a nucleus in Dy metal.

$\Delta\langle r^2 \rangle$ ( $10^{-3} \text{fm}^2$ )	$\rho_c(\text{O})$ Experimental	Theoretical
4.4 <sup>a</sup>	$3.960 \pm 0.188$	
7.3 <sup>a</sup>	$2.387 \pm 0.113$	0.695 <sup>b</sup>
9.5 <sup>a</sup>	$1.834 \pm 0.087$	
12.7 <sup>a</sup>	$1.372 \pm 0.065$	

<sup>a</sup>Cashion *et al* (1975) and references therein,

<sup>b</sup>Present calculation.

### 3. Theory

Using the APW method, the wave function for a conduction electron of wave vector  $\mathbf{k}$  and energy  $E$  can be written as

$$\psi_{\mathbf{k},E}(\mathbf{r}) = \frac{1}{F_{\mathbf{k},E}} \sum_n C_{\mathbf{k},E;n}(\mathbf{r}) \quad (2)$$

where

$$\begin{aligned} \phi_{\mathbf{k},E;n}(\mathbf{r}) = & \delta_1 \exp(i\mathbf{k}_n \cdot \mathbf{r}) + \delta_2 \exp(i\mathbf{k}_n \cdot \mathbf{r}_\mu) 4\pi \sum_{l,m} i^l [j_l(k_n \sigma)/R_1(E, \sigma)] \\ & \times Y_l^m(\mathbf{k}_n)^* Y_l^m(\mathbf{x}) R_1(E, x). \end{aligned} \quad (3)$$

Here  $\mathbf{k}_n = \mathbf{k} + \mathbf{K}_n$ ,  $\mathbf{K}_n$  being the  $n$ -th reciprocal lattice vector,  $\mathbf{x} = \mathbf{r} - \mathbf{r}_\mu$ ,  $\mathbf{r}_\mu$  being the position of the  $\mu$ -th atom in the lattice (here we assume that  $r$  lies within the Wigner-Seitz cell drawn around the  $\mu$ -th atom);  $\delta_1 = 0$ ,  $\delta_2 = 1$  for  $x < \sigma$  and  $\delta_1 = 1$ ,  $\delta_2 = 0$  for  $x > \sigma$ ,  $\sigma$  being the radius of the APW sphere;  $C_{\mathbf{k},E;n}$ 's are the coefficients of mixing of the APW functions corresponding to different  $\mathbf{K}_n$ 's in the total APW function and  $R_1$  is the solution of the radial part of the Schrödinger equation for the muffin-tin potential.  $F_{\mathbf{k},E}$  is the normalization constant and this is given by

$$F_{\mathbf{k},E}^2 = \sum_{n,n'} C_{\mathbf{k},E;n} C_{\mathbf{k},E;n'}^* \Delta_{n'n} \quad (4)$$

where

$$\Delta_{n'n} = \langle \phi_{\mathbf{k},E;n'} | \phi_{\mathbf{k},E;n} \rangle. \quad (5)$$

Hence the charge density at a point  $\mathbf{r}$  is

$$\rho(\mathbf{r}) = \sum_{\mathbf{k},E} \frac{1}{F_{\mathbf{k},E}^2} \sum_{n,n'} C_{\mathbf{k},E;n} C_{\mathbf{k},E;n'}^* \phi_{\mathbf{k},E;n} \phi_{\mathbf{k},E;n'}^*(\mathbf{r}). \quad (6)$$

The spherically-averaged charge density at distance  $r$  is given by,

$$\rho_c(r) = \frac{1}{4\pi} \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} \rho(\mathbf{r}) \sin \theta \, d\theta \, d\phi,$$

where  $r, \theta, \phi$  are the spherical polar coordinates of  $\mathbf{r}$ .

Therefore,

$$\begin{aligned} \rho_c(r) = & \sum_{l=0}^{\infty} (2l+1) \sum_{\mathbf{k},E} (1/F_{\mathbf{k},E}^2) [R_1^2(E, r)/R_1^2(E, \sigma)] \\ & \times \left[ \sum_{nn'} C_{\mathbf{k},E;n} C_{\mathbf{k},E;n'}^* j_l(k_n \sigma) j_l(k_{n'} \sigma) P_l(\cos \theta_{\mathbf{k}_n, \mathbf{k}_{n'}}) \right]. \end{aligned} \quad (7)$$

The above expression gives the charge density (inside the APW sphere) around the central ion.

### 4. Calculation and results

We have taken  $4f^{10}6s^2$  atomic configuration, lattice parameters  $a = 0.35903$  nm and  $c/a = 1.5730$ . The spin-polarization factor has been taken to be 0.5303. The non-relativistic atomic wave functions of Herman and Skillman (1963) have been used to

construct the crystalline potential. In the present spin-polarized band structure calculations of dysprosium metal the crystal potential has been constructed in the muffin-tin form considering the exchange and correlation parts in the von Barth and Hedin (1972) formalism. The effect of non-spherical part of crystal potential has not been taken into account as it has been shown (Mukhopadhyay and Das 1986) that this does not affect band structure significantly. The radius of the APW sphere has been found to be 3.1582 A.U. The energy band structures along the major symmetry axes for spin-up and spin-down electrons, calculated following the method of Loucks (1967), have been found to be similar in shape but one is shifted relative to the other; the average split being 0.022 Ry. Energy eigenvalues have also been calculated at sixty points distributed uniformly within  $1/24$ -th part of the Brillouin zone. Of these 60 points, 40 were general points each being equivalent to 24 and the remaining 20 were on symmetry lines each being equivalent to 12 points. So these 60 points are equivalent to 1200 points in the whole zone. The Fermi energy is found to be  $-0.4573$  Ry. It is found that the first two bands are completely filled and the next two are partly filled. These results have been reported elsewhere (Mukhopadhyay *et al* 1984). Figure 1 shows the spin-polarized energy bands and figures 2 and 3 show the density of states.

The experimental value of spin-splitting of 0.032 Ry obtained from the work of Cooper and Redington (1965) was matched by rigid shift of the spin-up band with respect to the spin-down band by 0.01 Ry; other quantities such as magnetic moment per atom, band width and density of states at the Fermi level have been evaluated and compared with experimental data. The results are shown in table 2. It is found that after the shift the agreement between the calculated magnetic moment per atom and its experimental value improves; the value of density of states at Fermi level,  $N(\epsilon_f)$  seems not to have improved but it may be noted that a direct comparison with experimental data obtained from specific heat measurement is not possible as this is enhanced due to electron-phonon and electron-magnon interactions.

The spherically averaged conduction electron densities for both spin-up and

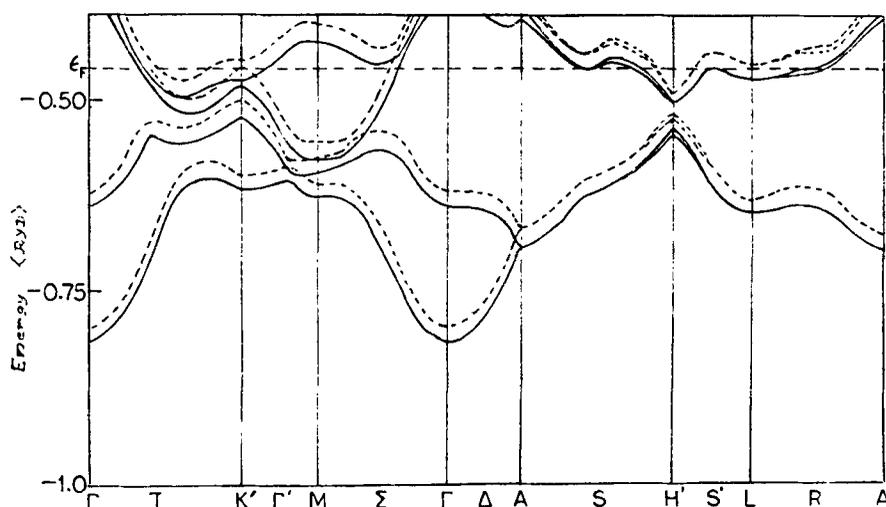


Figure 1. Energy bands in ferromagnetic dysprosium; spin-up bands —, spin-down bands - - - - -.

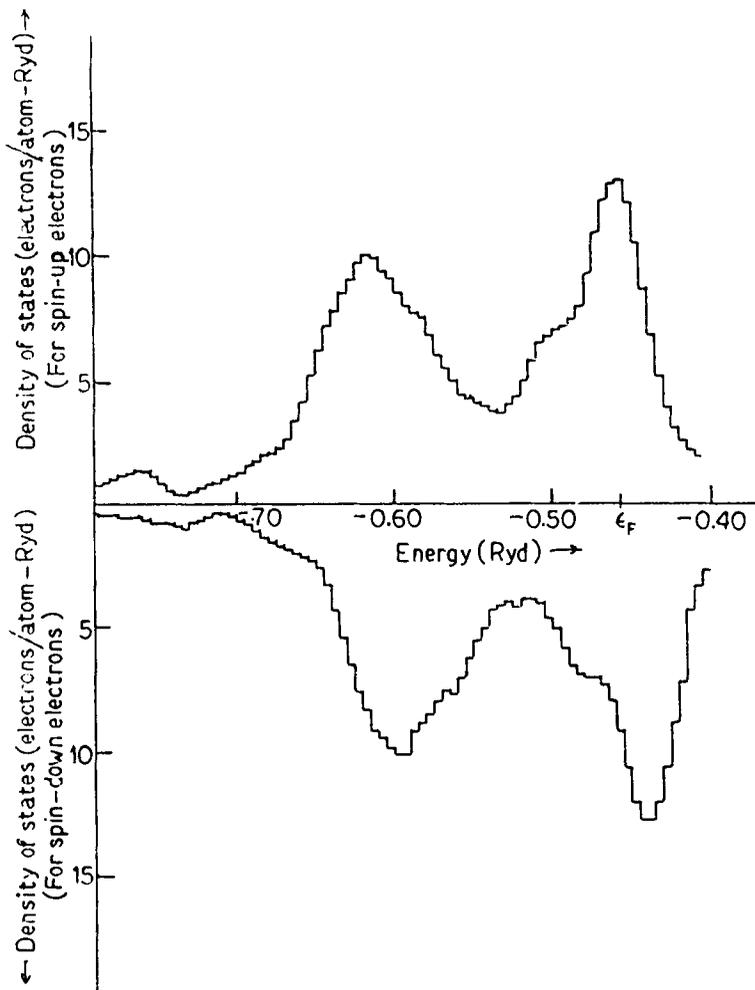
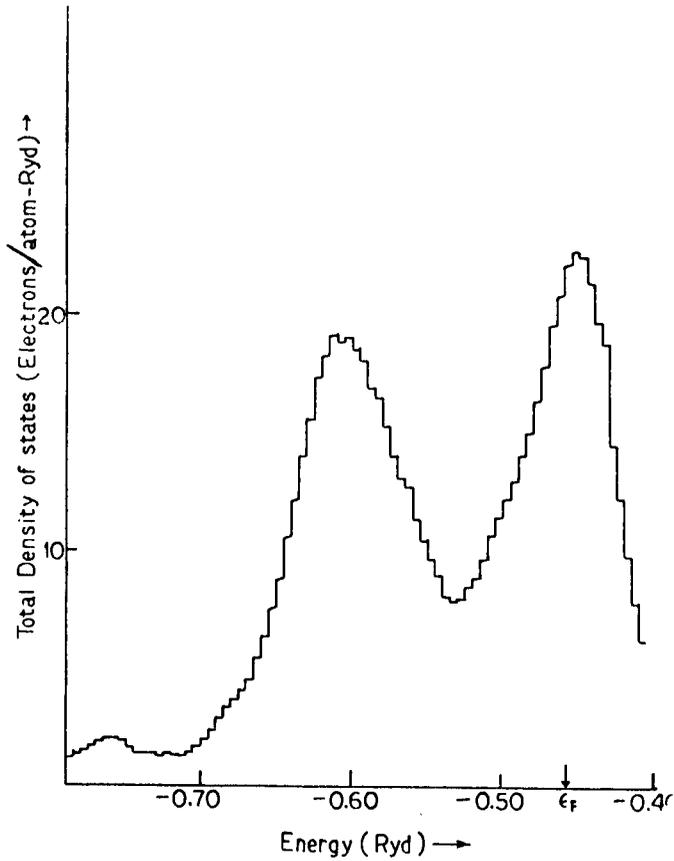


Figure 2. Spin-up and spin-down density of states histogram.

spin-down cases have been calculated using (7), and  $\rho_c(O)$  has been found to be  $0.695 \times 10^{26} \text{ cm}^{-3}$ .

## 5. Discussion

Belakhovsky and Ray (1975) in a tricky way obtained the product  $S'(Z)\Delta\langle r^2 \rangle$  as  $22 \times 10^{-3} \text{ fm}^2$  for dysprosium from a theoretical calculation of conduction electron density at the Dy-nucleus in the intermetallic compounds DyZn, DyCu and DyRh and the experimental values of isomer shifts in the respective cases. We get the product  $S'(Z)\Delta\langle r^2 \rangle$  as  $25 \times 10^{-3} \text{ fm}^2$  using (1) and our theoretical value of  $\rho_c(O)$ . It is observed that the value of the product is close to that obtained by Belakhovsky and Ray (1975). Taking  $S'(Z) = 3.99$ , the value recommended by Shirley (1964) for dysprosium atom we get  $\Delta\langle r^2 \rangle = 7.0 \times 10^{-3} \text{ fm}^2$  which is very close to  $7.3 \times 10^{-3} \text{ fm}^2$  as obtained by Cohen and West (1971).



**Figure 3.** Total density of states histogram.

**Table 2.** Experimental and theoretical values of different band structure parameters.

	Experimental	Theoretical	
		Before shift	After shift
Spin-splitting (Ry)	0.032 <sup>a</sup>	0.022	0.032 (matched)
Magnetic moment ( $\mu_B$ /atom)	0.41 <sup>b</sup>	0.28	0.37
$N(\epsilon_f)$ (electrons/ atom-Ry)	$28.3 \pm 0.5^c$	22.1	20.3
Bandwidth (Ry)	$0.404 \pm 0.015^d$	0.359	0.361

<sup>a</sup>Cooper and Redington (1965); <sup>b</sup>Lindgard and Danielsen (1975); <sup>c</sup>Hill and Gschneidner Jr (1988); <sup>d</sup>Lapeyre (1969).

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