Pramana - J. Phys., Vol. 37, No. 6, December 1991, pp. 513–524. © Printed in India.

Bloch enhancement of electric field gradient in Fe and Cu host alloys

P TRIPATHI and N C MOHAPATRA
Department of Physics, Berhampur University, Berhampur 760007, India

MS received 20 August 1991

Abstract. The Bloch enhancement factor $\alpha(\mathbf{k}_f)$ of the electric field gradient has been evaluated for the half-filled *d*-core Fe host metal and completely filled *d*-core Cu host metal in single orthogonalized plane wave (OPW) approximation. For this purpose the radially-dependent antishielding factors, $\gamma(r)$ have been calculated in non-orthogonal Hartree–Fock perturbation theory (NHFPT). The results show that the contributions of antishielding to $\alpha(\mathbf{k}_f)$ from the plane wave-plane wave part and the core part of the OPW state are individually large but opposite in sign and thereby lead to partial cancellation. The net effect of antishielding on $\alpha(\mathbf{k}_f)$ is found to be $-5{\cdot}6\%$ in Fe and 14% in Cu.

Keywords. Radial antishielding; Bloch-enhancement field-gradient; cubic host-metals.

PACS No. 31·20

1. Introduction

It is well known that when impurities and or point defects are introduced into an otherwise perfect cubic host solid, the cubic symmetry of the latter's charge distribution is lowered and a spatial distribution of electric field gradient (efg) results in the defect solid. The presence of defect atoms not only causes the valence electron distribution non cubic but also makes the ionic charge distribution non cubic by causing displacements in the ions from their equilibrium positions in perfect host solid. Ignoring the lattice displacements of ions it has been shown by both Blandin and Friedel (1960) and Kohn and Vosko (1960) that the efg due to a single defect atom in asymptotic limit can be expressed as

$$eq = (8\pi/3)e\alpha(\mathbf{k}_f)\Delta\rho(r) \tag{1}$$

where $e\Delta\rho(r)$ is referred to as the screening charge distribution (Alfred and Ostenburg 1967) and $\alpha(\mathbf{k}_f)$ as the Bloch enhancement factor (Kohn and Vosko 1960). While the former is dependent on the property of defect atom, the latter depends only on the properties of host lattice and is given by (Kohn and Vosko 1960)

$$\alpha(\mathbf{k}_f) = \frac{\int \mathrm{d}^3 r \psi^2(\mathbf{k}_f, \mathbf{r})(1-\gamma(r))/r^3 P_2(\cos\theta_{\mathbf{k}_f,\mathbf{r}})}{\int \mathrm{d}^3 r \exp(2i\cdot\mathbf{k}_f, r) P_2(\cos\theta_{\mathbf{k}_f,\mathbf{r}})/r^3} \tag{2}$$

$\psi_{\mathbf{k}_f}(r)$ is the wave function of conduction electron at the Fermi wave vector $\mathbf{k}_f$, $\gamma(r)$ is the radially-dependent antishielding factor (Sternheimer 1950 and Foley *et al* 1954)

of the core states of the host ion, P_2 is the Legendre polynomial of order 2 and $\theta_{\mathbf{k}_f, r}$ is the angle between the vector $\mathbf{k}_f$ and $\mathbf{r}$. It may be noted that in the work of Blandin and Freidel (1960) and Kohn and Vosko (1960), $\mathbf{k}_f$ is taken parallel to the direction of the host nucleus (measured from the defect atom) at which efg is evaluated.

The enhancement factor $\alpha(\mathbf{k}_f)$ has been evaluated by several authors using different approximations. In some calculations, ψ_{k_f} has been approximated by a single orthogonalized plane wave (OPW) and the effect of $\gamma(r)$ has been neglected. In the calculation of Fukai (1971) and of Fukai and Watanabe (1970, 1974), the single OPW state has been augmented by the inclusion of first order pseudopotential correction to the wave function. However, antishielding effect has been neglected in their calculation. In the calculation of $\alpha(\mathbf{k}_f)$ for Cu host, on the other hand, Kohn and Vosko (1960) have included the effect of $\gamma(r)$ and used the single OPW approximation. However, the $\gamma(r)$ used by the latter authors is slightly different from the present one. There is only one calculation (Holtham and Jena 1974) where Ψ_{k_f} has been represented by a sum of many OPW's and it has been determined in the band structure procedure of the host metal. While this is definitely a more accurate procedure than 1-OPW, yet in obtaining $\alpha(\mathbf{k}_f)$ the authors have neglected the antishielding effect completely. Considering the small core of Al, this neglect may be justified. But for larger core-host atoms like Cu and Fe the effect of antishielding may not be negligible. Some of the conclusions arrived at by the authors (Holtham and Jena 1974) are as follows. (a) The many OPW result is relatively close to the 1-OPW results (i.e. within 20%) and (b) the anisotropy of $\alpha(\mathbf{k}_f)$ with respect to different directions of $\mathbf{k}_f$ is within 10–20%.

For host atoms having larger core, the many OPW calculation will be more complicated and time-consuming than it is for Al. On the other hand the results from 1 OPW calculation are expected not to differ more than 20%. Keeping this fact and the conclusions of Holtham and Jena (1974) in view, we have carried out the calculation of $\alpha(\mathbf{k}_f)$ in Fe and Cu host metals in 1-OPW approximation. But while doing so we have included the antishielding effect of core states. The aim of the present work has been two-fold, namely (a) to extend the 1-OPW procedure to the half-filled *d*-core metal Fe for which $\alpha(\mathbf{k}_f)$ is not available and (b) to study the effect of antishielding on $\alpha(\mathbf{k}_f)$ in both Fe and Cu. Out of the two systems studied, Fe has a half-filled 3*d*-core with valence 3 and Cu has the completely-filled 3*d* core with valence 1. For both the ions $\gamma(r)$ have been calculated separately in non-orthogonal Hartree–Fock Perturbation Theory (NHFPT) and then used in the calculation of $\alpha(\mathbf{k}_f)$.

In §2, the theoretical procedure for the calculation of $\alpha(\mathbf{k}_f)$ has been briefly described. Results and discussions are presented in §3 and §4 summarizes the conclusions.

2. Theory

As $\alpha(\mathbf{k}_f)$ depends on $\gamma(r)$ and the latter has been calculated in the present work, we wish to briefly describe the NHFPT procedure, for the evaluation of $\gamma(r)$ in §2.1. In §2.2, the procedure for the calculation of $\alpha(\mathbf{k}_f)$ using $\gamma(r)$ will be described.

2.1 *Radially-dependent antishielding factor*

The theory for the radially-dependent antishielding factor, $\gamma(r)$ for ions was first formulated by Sternheimer (1950) and subsequently by Foley *et al* (1954) and by Rao

and Mohapatra (1981). The procedure followed by the latter authors and which is based on NHFPT will be briefly outlined here. The interested readers may refer to the work of Rao and Mohapatra (1981) for details. The expressions for $\gamma(r)$ is given by

$$\gamma(r) = 1/Q\left(\int_0^r Q_i(r')\mathrm{d}r' + r^5\int_r^\infty Q_i(r')(r')^{-5}\mathrm{d}r'\right), \tag{3}$$

where Q is the nuclear quadrupole moment and $Q_i(r')$ is the radial induced quadrupole moment density at r of the atomic core due to perturbation by nuclear Q. The induced density in radial mode of excitation is given by

$$Q_i(r) = Qr^2\sum_n c_{ll}^{(2)} P_{nl}(r)\, V_1'(nl\to l, r), \tag{4}$$

where $P_{nl}(r)$ is the radial part of the zero-order wave function characterized by the quantum number n and l and $V_1'(nl\to l)$ is the radial part of the first order perturbation to the wave function. $C_{ll}^{(2)}$ is a constant which results from the angular integration and summation over spin quantum number. For example, the value of $C_{ll}^{(2)}$ for completely $3d$-core state is 16/7 whereas for a half-filled d-core, its value is 8/7.

The functions $V_1'(nl\to l)$ are constructed from the non-orthogonal first order solution $V(nl\to l'r)$ by orthogonalizing the latter to all the zero order core states. The functions $V(nl-l,r)$ on the other hand are obtained as solutions of differential equations in NHFPT (see eq. (9) of Rao and Mohapatra (1981)). Similar expressions for $Q_i(r)$ due to angular mode of excitation exist, and these can be used to evaluate contribution to $\gamma(r)$ from angular mode. It may be noted here that the magnitude of angular contribution to $\gamma(r)$ is usually much smaller than the contribution from radial mode but takes more computation time for its determination. For this reason, a less realistic charge distribution, namely, a modified Thomas–Fermi (Rao and Mohapatra 1981) charge distribution is sometimes used for the angular contribution. In the present work the more important radial contribution has been evaluated by using zero-order Hartree–Fock wave functions of core states. The less important angular contribution, on the other hand, has been determined from a modified Thomas–Fermi model.

2.2 $\alpha(k_f)$ *in single OPW approximation*

In single OPW approximation, the conduction electron wave function corresponding to Fermi wave vector $\mathbf{k}_f$ is expressed as

$$\psi(\mathbf{k}_f,\mathbf{r}) = \mathrm{PW}(\mathbf{k}_f,\mathbf{r}) - \sum_i \langle\phi_i(\mathbf{k}_f)|\mathrm{PW}(\mathbf{k}_f)\rangle\phi_i(\mathbf{k}_f,\mathbf{r}), \tag{5}$$

where the plane wave, using the volume of normalization as 1 is given by

$$\mathrm{PW}(\mathbf{k}_f,\mathbf{r}) = \exp(i\mathbf{k}_f,\mathbf{r}) \tag{6}$$

and the core-wave function, each approximated by a single tight-binding function is

$$\phi_i(\mathbf{k}_f,\mathbf{r}) = 1/\sqrt{N}\sum_\mu \exp(i\mathbf{k}_f\cdot\mathbf{R}_\mu)U_i(\mathbf{r}-\mathbf{R}_\mu). \tag{7}$$

The functions $U_i(\mathbf{r}-\mathbf{R}_\mu)$ are atomic core functions located at the lattice site R_μ and

N is the number of atoms in the solid. In the approximation of zero overlap of atomic functions on different sites, the ϕ_i functions satisfy the orthonormality relation,

$$\langle \phi_i(\mathbf{k}_f) | \phi_j(\mathbf{k}_f) \rangle = \delta_{ij}. \tag{8}$$

The OPW function in (5) valid for closed shell atom needs to be generalized so as to be applicable to atoms with half-filled core states as in the case of Fe. In trivalent iron atom, the 3*d* core is half-filled with five electrons. We distribute these electrons paramagnetically among the ten substrates by allocating 0·5 electron to each. In such case the Bloch function describing a core electron in half-filled shell (e.g. 3*d* electron in Fe) would be represented by $1/\sqrt{2}\ \phi_i(\mathbf{k}_f, \mathbf{r})$ which is normalized to (1/2) as it should. With this representation of the core electron of a half-filled shell, the OPW of (5) can be generalized to

$$\psi(\mathbf{k}_f, \mathbf{r}) = \mathrm{PW}(\mathbf{k}_f, \mathbf{r}) - \sum_i \lambda_i \langle \phi_i(\mathbf{k}_f) | \mathrm{PW}(\mathbf{k}_f) \rangle \phi_i(\mathbf{k}_f, \mathbf{r}), \tag{9}$$

where the parameter λ_i assumes the value

$$\lambda_i = \begin{cases} 1 \text{ for each closed shell core state} \\ 0{\cdot}5 \text{ for each half-filled core state.} \end{cases} \tag{10}$$

The sum in (9) is taken over all the core states of closed and half-filled shells. In the case of atomic core functions, quantum number i stands for the set n, l, m. Now using (6) and (7) along with the standard expansion (Callaway 1974) of plane wave in spherical harmonics,

$$\exp(i\mathbf{k}_f, \mathbf{r}) = 4\pi \sum_{l'm'} (i)^{l'} Y^*_{l'm'}(\hat{k})\ Y_{l'm'}(\hat{r}) j_l(kr), \tag{11}$$

it can be shown that

$$\langle \phi_{nlm}(\mathbf{k}_f) | \mathrm{PW}(\mathbf{k}_f) \rangle = 1/\sqrt{\Omega} 4\pi (i)^l Y^*_{lm}(\mathbf{k}_f) I(nl, \mathbf{k}_f), \tag{12}$$

where Ω is the volume per atom, i is the imaginary number, $\sqrt{-1}$, $Y_{lm}(k_f)$ are the standard spherical harmonics corresponding to the polar angles of unit vector $\mathbf{k}_f$ and $I(nl, k_f)$ is the radial integral

$$I(nl, k_f) = \int_0^\infty P_{nl}(r) j_l(k_f r) r\, \mathrm{d}r. \tag{13}$$

The function $P_{nl}(r)$ is the normalized radial part of the atomic wave function and is related to the latter by

$$U_{nlm}(\mathbf{r}) = \frac{P_{nl}(r)}{r} Y_{lm}(\hat{r}). \tag{14}$$

With the help of (12) the normalization constant of $\psi(\mathbf{k}_f, \mathbf{r})$ of (9) can be expressed as

$$N^{-1/2}(k_f) = \left(1 - 4\pi/\Omega \sum_{n,l} (2\lambda_{nl} - \lambda_{nl}^2)(2l+1) I^2(nl, \mathbf{k}_f) \right)^{-1/2}. \tag{15}$$

By putting $\lambda_{nl} = 1$ for all the core states, the normalization constant of traditional OPW function (i.e. corresponding to closed shell core) can be reproduced.

In order to evaluate $\alpha(\mathbf{k}_f)$ from (2) for any general direction of $\mathbf{k}_f$, we express $P_2(\cos\theta_{\mathbf{k}_f,\mathbf{r}})$ in spherical harmonics following the standard expansion (Jackson 1967),

$$P_2(\cos\theta_{\mathbf{k}_f,\mathbf{r}}) = 4\pi/5 \sum_m Y_{2m}(\mathbf{k}_f)\, Y^*_{2m}(\hat{r}). \tag{16}$$

Using (16) and (11) in (2), the denominator of the latter can be easily shown to be $-4\pi/3$ (Holtham and Jena 1974). On the other hand, to evaluate the numerator of (2) we use (9) for $\psi(\mathbf{k}_f, \mathbf{r})$ and (16) for P_2 function. The resulting expression consists of contributions involving one atomic centre and multi atomic centre terms. The latter contribution is usually very small compared to the one centre contribution. This has been shown by Holtham and Jena (1974). In view of this we have made the approximation of retaining only one centre terms occurring in the expression of the numerator of (2). This has the effect of choosing the OPW function having only one atomic core at $\mathbf{R}_c = 0$ site. However, one should not make this approximation in the beginning as it would destroy the Bloch character of the said function.

With the above approximation we then separate the numerator of (2) into contributions arising from plane wave-plane wave (PW–PW), core–core (C–C) and plane wave-core (PW–C) part of the OPW. In simplifying the PW–PW contribution, we have made use of (11). For the C–C part, (12) along with the fact $N = 1/\Omega$ has been used. The PW–C part, on the other hand, has been simplified by using both (11) and (12). With the denominator equal to $-4\pi/3$, these contributions to $\alpha(\mathbf{k}_f)$ obtained by the above simplification are reproduced below

$$\text{PW–PW} = 3N^{-1}(\mathbf{k}_f) I_2(\mathbf{k}_f)$$

$$\text{C–C} = -(48\pi^2/5) N^{-1}(\mathbf{k}_f) \sum_{nl} \sum_{n'l'} \lambda_{nl}\lambda_{n'l'} I(nl, \mathbf{k}_f) I(n'l', \mathbf{k}_f)$$

$$\times J(nl, n'l') \sum_m \sum_{m'} \langle 2m + m' | lm | l'm' \rangle\, Y^*_{lm}(\mathbf{k}_f)\, Y^*_{l'm'}(\mathbf{k}_f)\, Y_{2m+m'}(\mathbf{k}_f) \tag{18}$$

and

$$\text{PW–C} = -(96\pi^2/5) N^{-1}(\mathbf{k}_f) \sum_{nl} \sum_{l} (i)^{l+l'} \lambda_{nl} I(nl, \mathbf{k}_f) K(nl, l', \mathbf{k}_f)$$

$$\times \sum_m \sum_{m'} \langle 2m + m' | lm | l'm' \rangle\, Y^*_{lm}(\mathbf{k}_f)\, Y^*_{l'm'}(\mathbf{k}_f)\, Y_{2m+m'}(\mathbf{k}_f) \tag{19}$$

where the quantities I_2, J and K (the integral I has been defined in (13)) stand for the radial integrals

$$I_2(k_f) = \int_0^\infty j_2(2\mathbf{k}_f r) \frac{1-\gamma(r)}{r} \mathrm{d}r \tag{20}$$

$$J(nl, n'l') = \int_0^\infty P_{nl}(r) P_{n'l'}(r) \frac{1-\gamma(r)}{r^3} \mathrm{d}r \tag{21}$$

and,

$$K(nl, l', k_f) = \int_0^\infty P_{nl}(r) j_{l'}(k_f r) \frac{1-\gamma(r)}{r^2} \mathrm{d}r, \tag{22}$$

and the quantity $\langle lm|l'm'|l''m''\rangle$ stands for the the angular integral

$$\langle lm|l'm'|l''m''\rangle = \int Y^*_{lm}(\hat{r})\, Y_{l'm'}(\hat{r})\, Y_{l''m''}(\hat{r}) \mathrm{d}\Omega(\hat{r}) \tag{23}$$

In (19), l' denotes the orbital angular momentum of different partial waves to which the plane wave of the OPW has been decomposed. The quantities $\langle lm|l'm'|l''m''\rangle$ for admissible values of orbital and magnetic quantum numbers are available in literature (Tinkham 1964).

Thus, one could evaluate $\alpha(\mathbf{k}_f)$ from (17)–(19) for any general direction of $\mathbf{k}_f$. In 1-OPW approximation the Fermi surface being spherical, $\alpha(\mathbf{k}_f)$ is isotropic, that is, $\alpha(\mathbf{k}_f) = \alpha(k_f)$. The latter value can be evaluated by averaging $\alpha(\mathbf{k}_f)$ over the spherical Fermi surface. That is,

$$\alpha(k_f) = (1/4\pi k_f^2) \int_{F.S} \alpha(\mathbf{k}_f) k_f^2 \, \mathrm{d}\Omega(k_f). \tag{24}$$

Now, substituting (17)–(19) in (24) and carrying out the angular integration over the direction of $\mathbf{k}_f$, we obtain using (23)

$$\begin{aligned}\alpha(k_f) = 3N^{-1}(k_f)\Bigg[I_2(k_f) + \Bigg\{ -4\pi/5 \sum_{nl}\sum_{n'l'} \lambda_{nl}\lambda_{n'l'}(i)^{l+l'} \\ \times I(nl, k_f) I(n'l', k_f) J(nl, n'l') + 8\pi/5 \sum_{nl}\sum_{l'} \lambda_{nl}(i)^{l+l'} \\ \times I(nl, k_f) K(nl, l', k_f) \Bigg\} \sum_m \sum_{m'} |\langle 2m + m'|lm|l'm'\rangle|^2 \Bigg]\end{aligned} \tag{25}$$

In (25) the first, second and the third term denote the contributions of the type PW–PW, C–C and PW–C respectively. While $l'm'$ refer to core quantum numbers for the C–C terms, they refer to the partial waves of the plane wave in the third term.

The rules of combination of angular momentum tell that the allowed values of the pair (l, l') for C–C contribution in d-core atoms are $(0, 2)$, $(2, 0)$, $(1, 1)$ and $(2, 2)$ which in spectroscopic notation are referred to as s–d, d–s, p–p and d–d terms respectively. Similarly, the allowed values of (l, l') (where l comes from core and l' from plane wave) of PW–C contribution are given in spectroscopic notations as s–d, d–s, p–p, p–f, d–d and d–g. These components have been calculated in the present work with a view to making comparison of their relative importance.

Before we switch to the next section we wish to state here the accuracy with which the radial integrals in (20)–(22) have been evaluated. The full range of integration in each case has been divided into two sub ranges, namely, $0 - r_{\max}$ and $r_{\max} - \infty$ where $r_{\max}$ is chosen to be much larger than the atomic radius R_c and at which the functions have negligible amplitudes and $\gamma(r)$ has attained its saturation value γ_∞. The contributions to the integrals J and K from the range $r_{\max} - \infty$ are expected to be small as the atomic functions in the integral have negligible amptitude in this region. On the other hand the contribution to I_2 integral from the range $r_{\max} - \infty$ is not negligible owing to long range of the plane wave function. Assuming $\gamma(r)$ equal to γ_∞ in the range $r_{\max} - \infty$, it has been shown in Appendix

$$I_2(k_f) = (1 - \gamma_\infty)/3 + \int_0^{r_{\max}} j_2(2k_f r)(\gamma_\infty - \gamma(r))/r \, \mathrm{d}r. \tag{26}$$

In the same appendix it has been shown that the contribution to J and K integrals from the range $r_{max} - \infty$ are of the order of $2^{-1} P_{nl}(r_{max}) P_{n'l'}(r_{max}) (1 - \gamma_\infty)/r_{max}^2$ and $2P_{nl}(r_{max}) (1 - \gamma_\infty)/k_f r_{max}^2$ respectively.

3. Results and discussion

We present our results in two parts. In the first part the results on $\gamma(r)$ are discussed and in the second part the results of $\alpha(\mathbf{k}_f)$ are discussed. Out of the two systems studied in the present work, Fe has a half-filled $3d$-core and Cu has all the cores completely filled. For calculating the radial contribution to $\gamma(r)$, we have used the zero-order Hartree–Fock wave functions, P_{nl} of Clementi (1965). These wave functions obtained for the neutral atom configuration are considered more appropriate for the metallic environment than those belonging to ionic configuration. The contribution to $\gamma(r)$ from radial model was calculated exactly from NHFPT using the above zero-order wave functions. For the contribution from angular mode, a less realistic

Table 1. Radially dependent antishielding factor $\gamma(r)$ of Fe^{3+} and Cu^+ (r is expressed in atomic unit).

Fe^{3+}		Cu^+	
r	$\gamma(r)$	r	$\gamma(r)$
0·0004	0·0000	0·0004	0·0000
0·0006	0·0000	0·0006	0·0000
0·0011	0·0000	0·0010	0·0000
0·0018	0·0001	0·0016	0·0001
0·0029	0·0003	0·0027	0·0002
0·0049	0·0006	0·0044	0·0005
0·0081	0·0012	0·0069	0·0010
0·0104	0·0018	0·0099	0·0017
0·0133	0·0026	0·0104	0·0018
0·0345	0·0110	0·0133	0·0028
0·0598	0·0277	0·0282	0·0083
0·1627	0·1502	0·0986	0·0780
0·2089	0·1691	0·1146	0·0979
0·2683	0·1691	0·1547	0·1411
0·2965	0·1459	0·2088	0·1533
0·4423	0·3817	0·4001	0·5339
0·7292	0·8816	0·8057	0·3211
0·9363	−0·4266	0·8470	0·0888
1·2023	−3·4125	1·2020	−4·4552
1·5438	−6·9499	1·7057	−9·6371
1·9822	−9·6415	2·9564	−15·7051
2·5422	−11·1084	3·9907	−17·2914
3·4357	−11·8731	4·8742	−17·6291
5·3883	−12·1740	7·1644	−17·6584
8·8837	−12·1911	9·8155	−17·6323
11·9920	−12·1912	10·8480	−17·6285
12·6070	−12·1912	11·4040	−17·6269
13·2530	−12·1912	11·9890	−17·6267
13·9320	−12·1912	12·6030	−17·6267

charge distribution, namely the one from modified T–F model was used in exactly the same way as in the work of Rao and Mohapatra (1981). Both the angular and radial contributions to $\gamma(r)$ have been calculated at 209 mesh points of r value chosen in a log scale, the r_{max} being different for Fe and Cu. The results of total $\gamma(r)$, (i.e. the sum of contributions from radial and angular modes) at some representative mesh points are given in table 1 for Fe^{3+} and Cu^{+} ions respectively. The respective value of r_{max} used in atomic unit is 13·932 and 12·603 for Fe^{3+} and Cu^{+}. The table clearly shows the saturation of $\gamma(r)$ around r_{max} in each case.

In the calculation of $\alpha(\mathbf{k}_f)$ the lattice constant for Fe and Cu lattice have been taken as 5·4065 a.u. and 6·8227 a.u. The Fermi wave vector $\mathbf{k}_f$ used in each case is the free electron value calculated for the trivalent Fe and monovalent Cu atom, the parameter λ_{nl} is set equal to 1 for all the core states of Cu and for the 1*s* through 3*p* core states of Fe. But for 3*d* core states of Fe, λ_{nl} is put equal to 0·5 as the latter core is half-filled.

The allowed values of all the angular integral $\langle lm|l'm'|l''m''\rangle$ except $\langle 2m+m'|2m|4m'\rangle$ are taken from Tinkham (1964) and the value of the latter has been evaluated using standard relation (Messiah 1965). The radial integrals I_2, J, K and I occurring in (25) have been evaluated by generating the respective integrands at the same 209 mesh points of the respective log scales as were used to calculate $\gamma(r)$ for Fe and Cu. The contributions to $\alpha(\mathbf{k}_f)$ from the PW–PW, C–C and PW–C parts have been separately calculated. The contribution from C–C and PW–C have been further separated into *sd*, *pp*, *dd*, *pf*, *dg* components as described in § 2.2. The results of $\alpha(\mathbf{k}_f)$ are presented in tables 2 and 3 for Fe and Cu respectively. In each of these tables the results of $\alpha(\mathbf{k}_f)$ calculated with and without $\gamma(r)$ are separately displayed.

Table 2. Contributions from various terms to $\alpha(k_f)$ in Fe. PW–PW, C–C and PW–C refer to contribution from plane wave–plane wave, core–core and plane wave–core parts of the OPW respectively *s–d*, *p–p*, *d–d*, *p–f* and *d–g* denote the corresponding angular momentum components in spectroscopic notation (see text I R and O R refer to inner $(O - r_{max})$ region and outer $(r_{max} - \infty)$ region respectively.

		$\gamma(r) \neq 0$	$\gamma(r) = 0$
	I R	6.784	
PW–PW	O R	−1·619	
	Total	5·165	1·437
	s–d	4·487	5·890
	p–p	32·865	35·382
C–C	*d–d*	−1·040	−1·242
	Total	36·312	40·030
	s–d	−1·412	−0·570
	p–p	−1·942	−0·162
	p–f	0·331	−0·019
PW–C	*d–s*	−6·136	−5·880
	d–d	1·125	0·331
	d–g	−0·212	−0·056
	Total	8·246	−6·356
Net $\alpha(k_f)$		33·231	35·111

Table 3. Contributions from various terms to $\alpha(k_f)$ in Cu, PW–PW, C–C and PW–C refer to contribution from plane wave–plane wave, core–core and plane wave–core parts of the OPW respectively *s–d*, *p–p*, *d–d*, *p–f* and *d–g* denote the corresponding angular momentum components in spectroscopic notation (see text). I R and O R refer to inner $(O - r_{max})$ region and outer $(r_{max} - \infty)$ region respectively.

		$\gamma(r) \neq 0$	$\gamma(r) = 0$
PW–PW	I R	12·497	
	O R	−2·303	
	Total	10·194	1·293
C–C	*s–d*	5·370	9·671
	p–p	18·574	20·322
	d–d	−2·856	−3·906
	Total	21·088	26·087
PW–C	*s–d*	−0·676	−0·408
	p–p	−0·846	−0·229
	p–f	−0·098	0·055
	d–s	−10·683	−9·772
	d–d	1·119	0·370
	d–g	−0·143	−0·081
	Total	−11·131	−10·065
Net $\alpha(k_f)$		20·151	17·315

The features of the results presented in tables 2 and 3 are: (a) the largest contribution to $\alpha(\mathbf{k}_f)$ is of $p - p$ type arising from C–C part, (b) the PW–PW contribution from outer region (i.e. $r_{max} - \infty$ region) is opposite in sign to the contribution from inner region $(0 - r_{max})$ and is by no means negligible, (c) the total change in contribution to $\alpha(\mathbf{k}_f)$ due to antishielding effect, which is composed of opposite contributions from the core states (i.e. the sum of contributions of C–C and PW–C) and plane wave state (i.e. PW–PW contribution) is negative for Fe and positive for Cu.

The *p*-states being the lowest angular momentum core states with the most aspherical charge distribution are expected to give the largest expectation value of the operator $P_2(\cos\theta)/r^3$. This explains the feature (a) above. With regard to feature (b) we are to state that due to the combined effect of the long range nature of plane wave states and the saturation value of $\gamma(r)$ in the outer region, the contribution to $\alpha(\mathbf{k}_f)$ from the latter region is finite and non-negligible. It may be noted that in a number of other calculations this contribution has been either neglected (Fukai 1971, Fukai and Watanabe 1970 and 1974) or has been estimated (Kohn and Vosko 1960) less accurately than from the present work. Because of cancellation the net antishielding effect referred to in (c) above is reduced in magnitude and is about −5·6% in Fe and 14% in Cu. The negative results in Fe is due to the smaller difference in the PW–PW contribution than in Cu.

The contribution to C–C and PW–C part from the outer region are negligible as the core functions have negligible amplitudes in this region. Following the approximation stated in the appendix, the contributions from the outer region to C–C and PW–C are estimated to be less than 10^{-5} and 10^{-11} respectively in both Fe and Cu.

Table 4. The values of J and I integrals for p-states in Fe and Cu. The results are in atomic units.

Atom	$J(2p,2p)$	$J(2p,3p)$	$J(3p,3p)$	$I(2p,k_f)$	$I(3p,k_f)$
Cu	635·21	−213·58	76·18	0·021	0·287
Fe	434·55	143·47	51·04	0·033	−0·446

Table 5. Contribution to $\alpha(k_f)$ in Cu computed from the atomic core region $(O - R_c)$ only. $R_c = 2{\cdot}544$ a.u.*, is the radius of the atomic sphere PW–PW, C–C and PW–C denote respectively the contributions from the plane wave–plane wave, core–core and plane wave–core parts.

	Present results				Results of Kohn and Vosko (1960)		
PW–PW	C–C	PW–C	Total	Outer region	I R	O R	Total
8·236	15·455	−4·495	19·196	0·955	23·3	2·3	25·6

*This value chosen in log scale is close to the actual $R_c = 2{\cdot}666\,309$ a.u.

Comparing the result of $\alpha(\mathbf{k}_f)$ of Fe with those of Cu, we note that the C–C and PW–C contribution in Fe are larger in magnitude than those in Cu. Out of these the $p - p$ type contribution of C–C is in particular significantly larger in Fe than in Cu. In order to see why it is so we have analysed the J and I integrals for the $2p$ and $3p$ states. The values of these integrals are displayed in table 4. It may be observed from this table that while the magnitude of J integrals are larger, but that of I integrals are smaller in Cu than in Fe. The p-functions in Cu are more localized than in Fe. Further, while the J-integrals are weighted by $1/r^3$, the I-integrals are weighted by r. This explains the above observation. It is the sum of the product of J and I integrals which make the $p - p$ contribution in Fe larger than in Cu. The PW–PW contribution in Cu is larger than it is in Fe. This is mainly due to larger antishielding factor of Cu than Fe.

Since results of $\alpha(\mathbf{k}_f)$ for Fe are not available from other calculations we compare only results of Cu with those of Kohn and Vosko (1960). It may be noted that these authors had used a different $\gamma(r)$ (Foley *et al* 1954; Sternheimer and Foley 1956) with slightly smaller magnitude than the one used in the present work. Besides, in their calculation the inner region was assumed to be the atomic sphere of radius $R_c (R_c = 2{\cdot}66$ a.u.) which is much smaller than r_{max} used in the present work. The contribution from the outer region was estimated by them (Kohn and Vosko 1960) to be 2·3 without stating the details and accuracy of estimation.

In order to compare the present results with those of Kohn and Vosko (1960) we have repeated our calculation for all the components of contributions choosing almost the same inner region as was used by them. The contribution from the outer region is then obtained by subtracting the inner region contribution from the total given in table 3. These results are summarized in table 5. The results of Kohn and Vosko (1960) have also been displayed in this table. It may be seen from table 5 that as against the present results of 19·196, the result of Kohn and Vosko (1960) is 23·3. The discrepancy may be attributed to the different values of $\gamma(r)$ and partly to a

different zero-order core wave functions used in their calculations. The core wave functions used by Kohn and Vosko (1960) were those of Hartree and Hartree (1936) and correspond to the ionic configuration of Cu^+. These wave functions being more localized than those used in the present work are expected to give a larger $\langle 1/r^3 \rangle$ value and hence a larger $\alpha(k_f)$ than obtained in the present work. It would not be meaningful to compare the contribution from the outer region without knowing the details of estimation in their work (Kohn and Vosko 1960).

4. Conclusions

The results of $\alpha(\mathbf{k}_f)$ obtained in single OPW approximation for the half-filled *d*-core Fe and the completely-filled core Cu show that the effect of antishielding is about $-5{\cdot}6\%$ in Fe and $14{\cdot}7\%$ in Cu. It is further concluded that while the contribution to $\alpha(\mathbf{k}_f)$ from outer region is negligible for the core states, it is not so for the plane wave state (i.e. PW–PW contribution) if $\gamma(r)$ is not neglected. It is hoped that the many OPW results in Fe and Cu may differ from the 1 OPW results by about 20% as it was in the case of Al (Holtham and Jena 1974).

Acknowledgements

One of the authors, (PT) expresses her gratitude to the CSIR, India for granting financial assistance in the form of senior research fellowship.

Appendix

The contributions from the outer region ($r_{max} - \infty$) to the integrals I_2, J and K of (20)–(22) are estimated here. The integral I_2 is split into two parts namely,

$$I_2(k_f) = \int_0^{r_{max}} j_2(2k_f r)\frac{1-\gamma(r)}{r}\mathrm{d}r + \int_{r_{max}}^{\infty} j_2(2k_f r)\frac{1-\gamma(r)}{r}\mathrm{d}r. \tag{A1}$$

In the range $r_{max} - \infty$, $\gamma(r)$ is nearly a constant, equal to its saturation value γ_∞. In view of this, the second integral can be written as

$$\int_{r_{max}}^{\infty} j_2(2k_f r)\frac{1-\gamma(r)}{r} = (1-\gamma_\infty)\int_{r_{max}}^{\infty} j_2(2k_f r)(1/r)\mathrm{d}r. \tag{A2}$$

Further,

$$\int_{r_{max}}^{\infty} j_2(2k_f r)(1/r)\mathrm{d}r = \left(\int_0^{\infty} j_2(2k_f r)(1/r)\mathrm{d}r - \int_0^{r_{max}} j_2(2k_f)(1/r)\mathrm{d}r\right), \tag{A3}$$

where the first integral on the right is a standard integral having value equal to 1/3. Putting this result in (A3) and using the resulting expression and (A2) in (A1), we obtain

$$I_2(k_f) = (1-\gamma_\infty)/3 + \int_0^{r_{max}} j_2(2k_f r)\frac{\gamma_\infty - \gamma(r)}{r}\mathrm{d}r, \tag{A4}$$

which is the result expressed in (26) of the text. The contribution to J integral from the outer region is approximated to

$$(1-\gamma_\infty)\int_{r_{max}}^{\infty} P_{nl}(r)P_{n'l'}(r)(1/r^3)\mathrm{d}r.$$

Since $P_{nl}(r)$ and $P_{n'l'}(r)$ are decaying exponentially in the above range, the magnitude of the above result is certainly less than

$$(1-\gamma_\infty)(P_{nl}(r_{max})P_{n'l'}(r_{max})\int_{r_{max}}^{\infty}(1/r^3)\mathrm{d}r,$$

which on integration leads to the inequality

$$\int_{r_{max}}^{\infty} P_{nl}(r)P_{n'l'}(r)\frac{1-\gamma(r)}{r^3}\mathrm{d}r < \frac{2^{-1}(1-\gamma_\infty)(P_{nl}(r_{max})P_{n'l'}(r_{max})}{r_{max}^2}. \tag{A5}$$

Following similar estimation, the contribution to K integral from the outer region can be approximated to

$$(1-\gamma_\infty)\int_{r_{max}}^{\infty} P_{nl}(r)j_{l'}(k_f)(1/r^2)\mathrm{d}r. \tag{A6}$$

In the outer range, $j_l(x) \sim \sin(x - l\pi/2)/x$ which can be further approximated to $1/x$. Including this in (A6) and following the same steps which led to (A5), it is easy to see that

$$\int_{r_{max}}^{\infty} P_{nl}(r)j_1(k_f)\frac{1-\gamma(r)}{r^2}\mathrm{d}r < \frac{2^{-1}(1-\gamma_\infty)P_{nl}(r_{max})}{k_f r_{max}^2} \tag{A7}$$

References

Alfred L C R and Van Ostenburg D O 1967 *Phys. Lett.* **A26** 27
Blandin A and Friedel J 1960 *J. Phys. Radium* **21** 689
Callaway J 1974 *Quantum theory of the solid state* (New York: Academic Press) p. 313
Clementi E 1965 *Tables of Atomic Functions* (New York: IBM)
Foley H M, Sternheimer R M and Tycko D 1954 *Phys. Rev.* **93** 734
Fukai Y 1971 *Phys. Lett.* **A34** 425
Fukai Y and Watanabe K 1970 *Phys. Rev.* **B2** 2357
Fukai Y and Watanabe K 1974 *Phys. Rev.* **B10** 3015
Hartree D R and Hartree W 1936 *Proc. R. Soc. (London)* **A157** 490
Holtham P M and Jena P 1974 *J. Phys.* **F5** 1649
Jackson J D 1967 *Classical electrodynamics* (New York: John Wiley) p. 68
Kohn W and Vosko S H 1960 *Phys. Rev.* **119** 812
Messiah A 1965 *Quantum mechanics* (New York: John Wiley) Vol. II p. 1057
Rao K K P and Mohapatra N C 1981 *Phys. Rev.* **A24** 10
Sternheimer R M 1950 *Phys. Rev.* **80** 102
Sternheimer R M and Foley H M 1956 *Phys. Rev.* **102** 731
Tinkham M 1964 *Group theory and quantum-mechanics* (New York: McGraw-Hill) p. 175