Electric field gradient in transition metal – scandium

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Abstract. Electric field gradient in *hcp* transition metal scandium has been calculated as the sum of contributions from lattice ions and conduction electrons. For the lattice contribution q_{latt}, a point-charge model has been assumed. The contribution from conduction electrons q_{el}, on the other hand, has been evaluated by carrying out an energy-band calculation using non-local transition-metal model potential. The results obtained are: $q_{el} = -106 \cdot 11 \times 10^{13}$ esu/cm^3 and $q_{latt} = 122 \cdot 17 \times 10^{13}$ esu/cm^3. The net field gradient $(q_{el} + q_{latt})$ of $16 \cdot 06 \times 10^{13}$ esu/cm^3 agrees quite well with the experimental result, $|q_{expt}| = 13 \times 10^{13}$ esu/cm^3. Directions of further improvement in the theory are discussed.

1. Introduction

It is now well-known [1, 2] that if conduction electron wave-functions are determined in the conventional crystal potential (i.e. its $l = 0$ component only), electric field gradient (EFG) due to these electrons would consist of two contributions: one from the anisotropic distribution of electrons in Fermi volume and the other from the perturbation of the Fermi surface electrons by the $l = 2$ component of the crystal potential. The latter, referred to as [1] as the Watson–Gossard–Yafet (WGY) mechanism [2], is particularly important for transition metals which have high density of electron states at Fermi-energy. The contribution to EFG from WGY mechanism is opposite in sign to the lattice contribution and may be as large as two or three orders of magnitude of the latter.

On the other hand, if model potentials are used in determining the band wave functions, the resulting EFG due to conduction electrons will be given exclusively by the electrons in the Fermi volume. This is because model potential parameters are determined by fitting with experimental data and the latter is expected to include the effect of the full crystal potential. As to the reliability of model potential calculations, it is well-known that using model potential, electronic properties of metals like phonon spectra, liquid metal resistivity, energy-bands, EFG's and a host of other properties have been predicted with reasonably good accuracy.

In the present calculation of EFG in *hcp* transition metal scandium, a non-local model potential has been used to determine the band wave functions. The motivation behind using a non-local model potential instead of a local potential is the following: EFG in a solid is sensitive to its potential distribution and the latter is non-local in character due to electronic exchange and correlation effects. A non-local model

potential is therefore expected to simulate the potential distribution in a metal better than a local model potential. The net EFG is expressed as a sum of lattice contribution q_{latt} and the conduction electron contribution q_{el}. The former is evaluated using the point-ion approximation [3, 4] for all the lattice ions except the one at whose nuclear site EFG is required. This is a good approximation in view of the fact that the overlap of the spherical cores of the distant ions with that of the ion in question is negligible. The effect arising from the deformation of the core of the ion in question by the distant ions and the nuclear quadrupole moment has been included through the Sternheimer antishielding factor [5]. But the contribution to EFG due to the deformed cores of the distant ions, which is expected to be small has been neglected. Unlike lattice contribution, the shielding/antishielding of electronic contribution is however very small [2] and in the absence of radially dependent antishielding factor $\gamma(r)$ [6] for Sc, it is estimated fairly accurately.

The results from the present calculation are compared with experiment as well as with other calculations [7–9]. The paper is organised as follows. In §2, the theory of electric quadrupole interaction in Sc is briefly described. Results and discussions are presented in §3 and §4 summarises the conclusions.

2. Theory

In Sc, the electrons in $1s$ through $3p$ orbitals are treated as core electrons and those in $3d$ and $4s$ are treated as conduction electrons. The model Hamiltonian expressed in atomic units (au) is given by

$$H = -\nabla^2 + V_m, \tag{1}$$

where V_m is the model potential. It consists of a local and a non-local part and has the form

$$V_m(E) = V_L - \sum_l A_l(E) P_l. \tag{2}$$

The parameters A_l as well as the model potential V_m are in general energy dependent. V_L is the local energy – independent part of the model potential and P_l is the standard angular momentum projection operator. The parameters A_l that are listed in literature [10] are however evaluated at Fermi energy E_f. But for the study of electronic properties of Fermi volume electrons, it is essential to use the energy dependent model potential. Therefore, to express $V_m(E)$ in terms of $V_m(E_f)$, we expand the former in a Taylor series about E_f. Retaining terms to first power in $(E - E_f)$ in the said expansion, we obtain

$$V_m(E) = V_m(E_f) + (E - E_f)(\partial V_m/\partial E)_{E_f}, \tag{3}$$

which in view of (2) reduces to

$$V_m(E) = V_L - \sum_l A_l(E_f) P_l - (E - E_f) \sum_l \left(\frac{\partial A_l}{\partial E}\right)_{E_f} P_l. \tag{4}$$

For narrow band metals the third term in (4) is expected to be negligible for two reasons. (1) The energy interval $E - E_f$ would be small and (2) the parameters A_l known to be slowly varying function of E [11] would remain almost constant in the

narrow energy range of occupied bands. Thus, for narrow band metals, one could approximate $V_m(E)$ as

$$V_m(E) \simeq V_L - \sum_l A_l(E_f)P_l. \tag{5}$$

i.e. one may use the same model parameters as evaluated at E_f for all the occupied energies in narrow band metals.

The model potential used in the present work is that of Animalu [10]. The corresponding screened form factor is expressed as the sum of a local V_L and non-local V_{NL} contribution. That is,

$$\frac{V(\mathbf{k} + \mathbf{K}, \mathbf{k} + \mathbf{K}')}{\varepsilon(|\mathbf{K}' - \mathbf{K}|)} = \frac{V_L(|\mathbf{K}' - \mathbf{K}|) + V_{NL}(\mathbf{k} + \mathbf{K}, \mathbf{k} + \mathbf{K}')}{\varepsilon(|\mathbf{K}' - \mathbf{K}|)}, \tag{6}$$

where

$$V_L(|\mathbf{K}' - \mathbf{K}|) = \frac{-4\pi d}{\Omega |\mathbf{K}' - \mathbf{K}|^3}\{\sin(|\mathbf{K}' - \mathbf{K}|R_m) - |\mathbf{K}' - \mathbf{K}|R_m \cos(|\mathbf{K}' - \mathbf{K}|R_m)\}$$

$$\frac{-8\pi Z}{\Omega |\mathbf{K}' - \mathbf{K}|^2}\cos(|\mathbf{K}' - \mathbf{K}|R_m)$$

$$+ \left\{\frac{4\pi}{\Omega}\frac{|Ec|}{|\mathbf{K}' - \mathbf{K}|^3} - \frac{24\pi Z\alpha_{\text{eff}}}{|\mathbf{K}' - \mathbf{K}|^5 R_c^3 \Omega}\right\}\{\sin(|\mathbf{K}' - \mathbf{K}|R_c)$$

$$- |\mathbf{K}' - \mathbf{K}|R_c \cos(|\mathbf{K}' - \mathbf{K}|R_c)\}, \tag{7}$$

and

$$V_{NL}(\mathbf{k} + \mathbf{K}, \mathbf{k} + \mathbf{K}') = \frac{-4\pi R_m^3}{\Omega(x^2 - y^2)}\sum_{l=0}^{2}(A_l - d)(2l + 1)P_l(\cos\theta_{\mathbf{k} + \mathbf{K}, \mathbf{k} + \mathbf{K}'})$$

$$\times \{yj_l(x)j_{l-1}(y) - xj_l(y)j_{l-1}(x)\}, \tag{8}$$

In (7) the last line is the contribution to local potential arising from correlation and orthogonalization correction [10]. x and y occurring in (8) stand for $|\mathbf{k} + \mathbf{K}|R_m$ and $|\mathbf{k} + \mathbf{K}'|R_m$ respectively. $j_l(x)$ is the spherical Bessel function of order l. The parameter $d = (2Z/R_m)$ and Z is the valency of the ion. The values of all the other parameters are given in [10]. The dielectric function ε used in the present work for screening the bare ion form factor is given [10] by

$$\varepsilon(q) = 1 + \frac{6\pi Z(1 + \alpha_{\text{eff}})}{\Omega E_f q^2}\left\{1 - \frac{q^2}{2(q^2 + k_f^2 + 2k_f/\pi)}\right\}$$

$$\times \left[1 + \frac{1}{2}\frac{1 - (q/2k_f)^2}{(q/2k_f)}\log\left|\frac{1 + q/2k_f}{1 - q/2k_f}\right|\right], \tag{9}$$

where k_f is the Fermi wave vector. It may be remarked here that the screening of the bare ion model potential by dielectric constant of the valence electron gas builds into the procedure the self-consistency of electron potential to a large extent.

The model wave function χ_n is expanded in a basis of plane waves,

$$|\chi_n(\mathbf{k})\rangle = \sum_{\mathbf{K}} C_n(\mathbf{k} + \mathbf{K})|PW(\mathbf{k} + \mathbf{K})\rangle. \tag{10}$$

The band energies $E_n(\mathbf{k})$ and the coefficients $C_n(\mathbf{k} + \mathbf{K})$, where n is the band index,

are determined as solutions of the secular equation,

$$|H_{k+K, k+K'} - E_n(k)\delta_{K K'}| = 0. \tag{11}$$

The true wave function $\Psi_n(k, r)$ is constructed from the corresponding model wave function $\chi_n(k, r)$ by orthogonalising the latter to the core states. That is,

$$|\Psi_n(k)\rangle = \sum_K C_n(k + K)[|PW(k + K)\rangle - \sum_t \langle\phi_t(k)|PW(k + K)\rangle\phi_t(k)\rangle], \tag{12}$$

where $\phi_t(k, r)$ is the tight-binding (TB) function representing the tth core state in metal and $\langle\phi_t(k)|PW(k + K)\rangle$ is the orthogonalisation coefficient.

The contribution to EFG from the conduction electrons is calculated using the relation [4],

$$q_{el} = -\sum_{nk} \int \Psi_n^*(k, r)\frac{3\cos^2\theta - 1}{r^3}[1 - \gamma(r)]\Psi_n(k, r)d^3r, \tag{13}$$

where the negative sign is a consequence of the negative charge on electron. r and θ refer to the nucleus in question as the origin and the c-axis as the z direction. The sum in (13) is taken over the occupied bands at the reduced wave vector k in the Brillouin Zone (BZ).

The lattice contribution, on the other hand, is evaluated using the standard expression [3, 4],

$$q_{latt} = Z(1 - \gamma_\infty)[0.0065 - 4.4584(c/a - 1.633)]/a^3, \tag{14}$$

which results from summing over the ionic EFG due to all the distant point-ions located at the lattice sites. Z and γ_∞ in (14) denote the valency and Sternheimer antishielding factor respectively and c and a are lattice parameters of the hcp crystal.

The factor $1 - \gamma(r)$ in (13) shields the electronic contribution. This would have negligible effect on the contribution arising from the part involving TB function of $\Psi_n(k, r)$. This is because in the region where the amplitude of core functions is large, $\gamma(r)$ is negligible and in the region where $\gamma(r)$ is large, the amplitude of core function is negligible. On the other hand, the effect of shielding on plane wave contribution is likely to be significant because of the long range nature of plane wave states and the saturation value of $\gamma(r)$ at large distance.

3. Results and discussion

The lattice parameters $a = 6.2391$ au and $c = 9.9316$ au are taken from the work of Das [12]. The model potential parameters used are those of Animalu [10]. Energies and band wave functions are calculated at 3456 representative k points chosen throughout the full BZ. For this purpose, in each of the 1/24th irreducible part of BZ, 144 k points distributed suitably over nine equidistant planes sliced perpendicular to c-axis are chosen. To each of these k points a weight factor in proportion to the volume it represents is assigned. Accuracy of EFG with respect to variation in the number of k points has been tested and found good to within 1% for the number of k points chosen in the present work. At each k point the model wave function $\chi_n(k, r)$

is expanded in 23 plane waves corresponding to the shortest 23 wave vectors $|\mathbf{k} + \mathbf{K}|$ for that $\mathbf{k}$ point. Thus the size of the matrix diagonalised at each $\mathbf{k}$ point is 23×23. With this choice the convergence of energy and eigen function is found good. For this purpose energies of occupied bands were calculated by varying the size of the matrix successively and the corresponding rate of changes in energy were noted. With 23×23 matrix the bands have converged to within 0·001 Ry.

The difference between E_f and the energy of the lowest occupied band at most of the representative $\mathbf{k}$ points chosen in the present work is found to be less than 0·5 Ry. This justifies the narrow band approximation in Sc.

The shape of energy bands calculated at symmetry points in the present work is compared with the one obtained by Das [12]. Except for the absolute value of energy, the shape of the band structure agrees fairly well with that of Das [12]. The difference in the absolute values of energy at any given symmetry point is attributed to the different choices of the zero of energy scale in both the calculations. The density of states at Fermi energy in the present work is about 9 states Ry^{-1} atom^{-1}. This is somewhat lower than the value obtained by Das [12]. This may suggest that the contributions to specific heat from lattice phonons and electron paramagnon interaction in Sc are more important than the electronic contribution at the temperature $(11°\text{K})$ considered.

Since $\gamma(r)$ for Sc is not available, the unshielded value of q_{el} (i.e. by putting $\gamma(r) = 0$) has been calculated from (13). As pointed out in § 3, this would not however affect the contribution involving tight-binding part of $\Psi_n(\mathbf{k}, \mathbf{r})$. It would only affect the pure plane wave (PW–PW) contribution. An estimation for the shielded PW–PW contribution will be discussed later.

The total electronic contribution is divided into the components of the type PW–PW, $s - d$, $p - p$, $p - f$ and distant. While the term PW–PW arises from the pure plane wave part of $\Psi_n(\mathbf{k}, \mathbf{r})$, $s - d$, $p - p$ and $p - f$ arise from the non-plane wave (i.e. TB–TB, PW–TB and TB–PW) part. The latter contributions result from the allowed angular momentum components [4] and are denoted in spectroscopic notations. The 'distant' type contribution, on the other hand, represents the contribution from the $l = 0$ component of the electronic charge distribution centred on ions other than the one in question. Details about this contribution can be found in [13].

The various components of q_{el} (unshielded) obtained by taking the weighted sum of the contributions from all the occupied bands at each of the representative $\mathbf{k}$ points in the full BZ are displayed in table 1. The lattice contribution q_{latt} as well as experimental result [7, 14] and the theoretical result from Blaha *et al* [7] are also listed in this table. In obtaining the lattice contribution the value of $\gamma_\infty (= -23·104)$ for Sc is taken from the work of Schmidt *et al* [15]. The latter result obtained by using Watson sphere model approximation [15] for the crystal potential would be more appropriate for solid state calculations than the free-ion γ_∞. Besides, it also includes the contribution from electron self-consistency effect, a contribution which is often neglected in other works. In view of these facts γ_∞ used in the present work is expected to be quite accurate. The core functions used in the present work are those of Clementi [16].

Column 3 in table 1 gives the shielded PW–PW contribution, whose estimation is discussed later. Columns 10 and 11 list the net unshielded and shielded EFG respectively. From this table, one notes that among the unshielded contributions, the dominant is the $p - p$ term. This is understandable because the most asymmetric state with the lowest l is the p state. Next bigger contribution is the $s - d$ term. This

Table 1. Various components of EFG in *hcp* scandium metal. All the EFG's are expressed in units of 10^{13} esu/cm^3.

| q_{latt} | Present work | | | | | | | | | | Other work* q | Expt. $|q|$ |
| | q_{el} | | | | | | | | | | | |
	PW–PW unshielded	PW–PW shielded	$s-d$	$p-p$	$p-f$	dist.	Total (unshielded)	Total (shielded)	Net q Colm. 1 + Colm. 8	Net q Colm. 1 + Colm. 9		
122·17	−0·63	−7·91	−4·72	−91·98	−1·31	−0·19	−98·83	−106·11	23·34	16·06	32·0	13·0

*Blaha et al [7]

arises from the *s* part of TB function and the *d* part of plane wave states. The net q_{el} is of opposite sign to q_{latt} and thus screens the latter. The net field gradient (unshielded) comes to $23 \cdot 34 \times 10^{13} \text{esu/cm}^3$.

We now wish to present the estimation for the shielded PW–PW contribution. For this purpose we refer to the Mahapatra *et al* [4] on the EFG in Cd and Zn. In their work, it was shown that the maximum shielding (antishielding) of PW–PW contribution will be by a factor $(1 - (\gamma_\infty/2))$. This is supported by a recent calculation [17] in which free-ion $\gamma(r)$ has been used to evaluate the shielded PW–PW contribution in Fe and Cu metals. The exact shielding factor obtained [17] for Fe and Cu are respectively $3 \cdot 59$ and $7 \cdot 88$, which are smaller than $6 \cdot 6$ and $9 \cdot 3$, the respective values of $1 - (\gamma_\infty/2)$ for Fe and Cu. As $\gamma(r)$ for Sc is not available, we have assumed the shielding factor to be $1 - (\gamma_\infty/2)$. Using the latter, the shielded PW–PW contribution comes to $- 7 \cdot 91 \times 10^{13} \text{esu/cm}^3$ and the total electronic contribution comes to $- 106 \cdot 11 \times 10^{13} \text{esu/cm}^3$. Adding q_{latt} to the latter would give the net EFG equal to $16 \cdot 06 \times 10^{13} \text{esu/cm}^3$ (colm. 11), which agrees quite well with experiment [7]. It is true that some inaccuracy has crept in by using the approximate shielding factor $1 - (\gamma_\infty/2)$. But surely, the exact factor cannot exceed $1 - \gamma_\infty$, the limiting value of antishielding by a distant ion. With a view to finding how much the net EFG would become if $1 - \gamma_\infty$ is used in place of $1 - (\gamma_\infty/2)$, we have recalculated the shielded PW–PW contribution using $1 - \gamma_\infty$. This leads to a net EFG of $8 \cdot 78 \times 10^{13} \text{esu/cm}^3$. Therefore, considering the uncertainty in the shielding factor the present result may be stated to lie anywhere between $8 \cdot 78 \times 10^{13} \text{esu/cm}^3$ (corresponding to shielding by $1 - \gamma_\infty$) and $23 \cdot 34 \times 10^{13} \text{esu/cm}^3$ (corresponding to no shielding). That is, the present result may be quoted as, $q = (16 \cdot 06 \pm 7 \cdot 28) \times 10^{13} \text{esu/cm}^3$. It may be noted that the experimental value [7] of q falls in this range.

Now we compare the present results with those calculated by Blaha *et al* [7]. They had used the full potential linearized augmented-plane-wave procedure to calculate EFG in a number of *hcp* metals including Sc. The net EFG in their work [7] for Sc is $+ 32 \times 10^{13} \text{esu/cm}^3$ which differs considerably from experiment and also from the present result. The dominant term in their work is $p - p$ as it is in the present work but with the following difference. The magnitude of $p - p$ contribution in their work is about one-half of the present result and the sign is opposite. This may have something to do with their partitioning of core electrons into semi-core and true-core states and treating the semicore electrons (namely, $3s$ and $3p$ states in Sc) as completely band states. The convergence of the band wave functions corresponding to the $3s$ and $3p$ is normally not very good unless one uses a relatively large number of basis functions. This aspect needs some re-examination. Further it seems that a factor of 2 is missing on the right hand side of (2) in their work [7]. If it is not due to typographical omission, their results would change by this factor making agreement with experiment worse.

The authors [7] of LAPW procedure claim that they have considered all charges including nuclear charges for determining the potential. It is however not clear as to whether the non-spherical nature of nuclear charge distribution has been duly taken note of in their work. If not, the quadrupole moment of nuclear charge would perturb both the true-core and semi-core states in their work to give additional contribution to EFG through Sternheimer antishielding mechanism. These contributions, particularly the ones from $2p$ and $3p$ states are likely to be significant. The present work does include these contributions.

Another difference one notices between the present result and those of Blaha *et al*

[7] is in regard to the magnitude of lattice contribution to EFG. While the latter contribution is significant in the present work, it is negligible in their work. This difference may be attributed to the different ways of partitioning the electrons in two procedures. Whereas in the present work, $1s$ through $3p$ states, treated as core states, contribute to lattice EFG, in LAPW procedure, $1s$ through $2p$ states, treated as true-core contribute to lattice and $3s - 3p$, treated as semi-core states, contribute to valence EFG. If the latter contributions $(3s - 3p)$ in LAPW procedure are calculated in the presence of nuclear quadrupole moment (which is perhaps not done) and added to lattice EFG instead of valence, the resulting lattice contribution may not be negligible. The reason for treating $3s$ and $3p$ as core states in the present work is their small and negligible overlap on nearest neighbour atoms in Sc metal. The calculated overlap of atomic $3p$ orbital on nearest neighbour atom in Sc is found to be less than 0·02%. We consider this to be negligible enough to regard $3p$ and also $3s$ as non-overlapping core states.

The sign of q from experiment [14, 7] is not available. We wish to remark here that irrespective of the sign of experimental q, the present result would be more close to experiment than those of Blaha *et al* [7]. Before we conclude this section we wish to suggest the following refinements in the present theory.

1] The band wave functions be redetermined in an energy dependent model potential of the form given in (3). This would not only give more accurate q_{el} than obtained at present but also throw light on the validity of approximation leading to (5) in narrow band metals.

2] Radially dependent antishielding factor $\gamma(r)$ appropriate for solid state be calculated so that using the latter the shielded (PW–PW) contribution to EFG be evaluated more accurately than estimated here.

In addition, fresh attempts be made in the experimental side to determine the sign of EFG so that it would serve as a more positive yardstick to assess the accuracy of theoretical calculations.

4. Conclusions

We conclude that by using a non-local transition metal model potential for the energy band calculations in Sc, the net EFG calculated as the sum of lattice and conduction electron contributions agrees quite well with experiment. This not only reaffirms confidence in the use of model potential for the study of such electronic properties in metals but also provides indirect support to the accuracy of point-ion approximation for the lattice contribution. Further, we hope that the present results would improve in the right direction if $\gamma(r)$ is used for obtaining the shielded (PW–PW) contribution.

References

[1] P Jena, S D Mahanti and T P Das, *Phys. Rev.* **B7**, 975 (1973)
[2] R E Watson, A C Gossard and Y Yafet, *Phys. Rev.* **140**, A375 (1965)
[3] M Pomerantz and T P Das, *Phys. Rev.* **123**, 2070 (1961)
[4] N C Mohapatra, P C Pattnaik, M D Thompson and T P Das, *Phys. Rev.* **B16**, 3001 (1977)
[5] R M Sternheimer, *Phys. Rev.* **130**, 1423 (1963)
[6] K K P Rao and N C Mohapatra, *Phys. Rev.* **A24**, 10 (1981)
[7] P Blaha, K Schwartz and P H Dederichs, *Phys. Rev.* **B37**, 2792 (1988)
[8] B Drittler, M Weinert, R Zeller and P H Dederichs, *Phys. Rev.* **B42**, 9336 (1990)

[9] R Coehoorn and K H J Buschow, *Phys. Rev.* **B42**, 4645 (1990)
[10] A O E Animalu, *Phys. Rev.* **B8**, 3542 (1973)
[11] I V Abarenkov and V Heine, *Philos. Mag.* **12**, 529 (1965)
[12] S G Das, *Phys. Rev.* **B13**, 3978 (1976)
[13] N C Mohapatra, C M Singal, T P Das and P Jena, *Phys. Rev. Lett.* **29**, 456 (1972)
[14] E N Kaufmann and R J Vianden, *Rev. Mod. Phys.* **51**, 161 (1979)
[15] P C Schmidt, K D Sen, T P Das and A Weiss, *Phys. Rev.* **B22**, 4167 (1980)
[16] E Clementi, *Tables of atomic functions* (New York: IBM, 1965)
[17] P Tripathi and N C Mohapatra, *Pramana – J. Phys.* **37**, 513 (1991)