PRAMANA
— journal of
physics

Vol. 43, No. 5,
November 1994
pp. 391–400

Electronic contribution to electric field gradient in β-gallium

B K ACHARYA and N C MOHAPATRA*
Department of Physics, Govt. Science College, Chatrapur 761 020, India
*Department of Physics, Berhampur University, Berhampur 760 007, India

MS received 27 June 1994; revised 30 September 1994

Abstract. Electronic contribution to electric field gradient (EFG) in β-Ga has been calculated for the first time using the band wave functions. The results show that the magnitudes of the quadrupole resonance frequency and the net EFG agree with experiment to within 7% and 2% respectively.

Keywords. Electric field gradient; β-gallium; model potential.

PACS No. 76·60

1. Introduction

There has been extensive experimental investigation of quadrupole interaction in the solid phase of β-Ga. Pure quadrupole resonance frequency and its temperature variation are available [1–2] from nuclear quadrupole resonance experiments. The sign of EFG has also been predicted indirectly from the experimental and theoretical values of quadrupole anomaly [3–4]. In contrast to this, very little work has been done in theory to understand the quadrupole interaction in β-Ga. The only theoretical work available in literature [5–6] pertains to the evaluation of the ionic contribution to EFG in this solid. The latter is negative in sign [6] and is only a small per cent of the experimental EFG. This suggests that the electronic contribution must be quite significant.

While energy band calculations in β-Ga using pseudopotential [7] and augmented plane waves [8] are available, evaluation of the EFG using the band wave functions from these calculations has not been carried out. Nor are there calculations of EFG in β-Ga using the more recent methods, like the molecular clusters [9] and the full potential-linearized-augmented-plane waves procedures [10]. It is this deficiency which has motivated us to carry out an energy band calculation for the evaluation of the electronic contribution to EFG in β-Ga.

A non-local model potential has been used to obtain the band energy and eigen functions in the Brillouin Zone (BZ). The cartesian components of the EFG tensor are then evaluated using these wave functions. The net EFG tensor obtained as a sum of contributions from lattice ions and conduction electrons is diagonalized to give the principal z-component and the asymmetry parameter. A comparison with experiment shows that the magnitudes of the calculated resonance frequency and the net EFG agree with experiment to within 7% and 2% respectively. There is however discrepancy with respect to the sign of the net EFG and the magnitude of the asymmetry parameter. Plausible explanations are offered for the existing discrepancy.

The paper is organized as follows. In §2, the theory of electric quadrupole interaction in β-Ga is briefly described. Results and discussions are presented in §3. Section 4 summarizes the conclusions.

2. Theory

The study of crystal structure of β-Ga [11] reveals that its unit cell is monoclinic and contains four atoms. The primitive cell, on the other hand, contains two atoms per cell. The lattice parameters [6] at 248 K are, $a = 2{\cdot}766$ Å, $b = 8{\cdot}053$ Å, $c = 3.332$ Å and $\beta = 92°03'$. For evaluating the components of EFG tensor, cartesian axes are set up such that the y and z axes are respectively in the directions of **b** and **c** crystal axes. The x-axis is then fixed from the requirement that x, y, z form a right-handed system. The symmetry of the crystal lattice combined with the above mentioned choice of cartesian axes predicts zero value for the cartesian components, q_{xy} and q_{yz} of the EFG tensor. This leaves only q_{xx}, q_{zz} and q_{xz} components of the traceless symmetric tensor to be determined. The lattice-ion contribution to these components, evaluated in the point-ion approximation, are taken from the work of Lodge [6] after making certain modifications which are described later. Atomic units (au), where $e^2 = 2$, $\hbar = 1$ and $m = 1/2$ have been used throughout in the calculation unless stated otherwise.

For the electronic contribution to EFG an energy band calculation has been carried out using a non-local model potential [12]. The band energies $E_n(\mathbf{k})$ and the eigen functions are obtained as solution of the secular equation,

$$|H_{\mathbf{k}+\mathbf{K},\mathbf{k}+\mathbf{K}'} - E_n(\mathbf{k})\delta_{\mathbf{K}\mathbf{K}'}| = 0, \tag{1}$$

where the matrix element of the model Hamiltonian H in a plane wave basis is given by

$$H_{\mathbf{k}+\mathbf{K},\mathbf{k}+\mathbf{K}'} = |\mathbf{k}+\mathbf{K}|^2\delta_{\mathbf{K}\mathbf{K}} + V(\mathbf{k}+\mathbf{K}, \mathbf{k}+\mathbf{K}'). \tag{2}$$

The second term in (2) is the Fourier transform of the non-local model potential, **k** and **K** are the wave vector in the *BZ* and the reciprocal lattice vector respectively. The model wave function χ, expanded in a plane wave basis with coefficients $C_n(\mathbf{k}, \mathbf{K})$ determined variationally is written as

$$\chi_n(\mathbf{k}, \mathbf{r}) = \sum_{\mathbf{K}} C_n(\mathbf{k}, \mathbf{K})\,\mathrm{PW}(\mathbf{k}+\mathbf{K}, \mathbf{r}) \tag{3}$$

where PW is the normalized plane wave,

$$\mathrm{PW}(\mathbf{k}+\mathbf{K}, \mathbf{r}) = \frac{1}{\sqrt{N\Omega}} \exp(i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}) \tag{4}$$

with N and Ω being the number of atoms in the solid and the volume per atom respectively.

By orthogonalizing χ_n to the crystal core states, each of which is represented by a single tight-binding function ϕ_j, the band wave function Ψ_n is obtained as

$$\Psi_n(\mathbf{k}, \mathbf{r}) = \sum_{\mathbf{K}} C_n(\mathbf{k}, \mathbf{K}) \left[\mathrm{PW}(\mathbf{k}+\mathbf{K}, \mathbf{r}) - \sum_j \langle \phi_j(\mathbf{k}) | \mathrm{PW}(\mathbf{k}+\mathbf{K}) \rangle \phi_j(\mathbf{k}, \mathbf{r}) \right] \tag{5}$$

The tight binding function for the jth core state is defined by

$$\phi_j(\mathbf{k},\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mu} \exp(i\mathbf{k}\cdot\mathbf{R}_\mu) u_j(\mathbf{r}-\mathbf{R}_\mu), \tag{6}$$

where $\mathbf{R}_\mu$ is the direct lattice vector and u_j is the jth atomic core function.

The cartesian components of EFG tensor due to the band electrons may be evaluated using the standard [13] relation,

$$q_{ij} = -\sum_{n,\mathbf{k}} \int \Psi_n^*(\mathbf{k},\mathbf{r}) \frac{\hat{q}_{ij}}{r^3} \Psi_n(\mathbf{k},\mathbf{r})[1-\gamma(r)]\,\mathrm{d}^3 r, \tag{7}$$

where $\gamma(r)$ is the radially dependent antishielding factor [14], $\hat{q}_{ij}$ is the angular operator of the ij-component of the EFG tensor. The sum in (7) is taken over all the occupied bands n at the $\mathbf{k}$ points in the BZ and the negative sign is due to the negative charge on electron. The angular operators $\hat{q}_{xx}$, $\hat{q}_{zz}$ and $\hat{q}_{xz}$, for example, are given [6] by

$$\begin{aligned} \hat{q}_{xx} &= 3\sin^2\theta\cos^2\phi - 1 \\ \hat{q}_{zz} &= 3\cos^2\theta - 1 \\ \hat{q}_{xz} &= 3\sin\theta\cos\theta\cos\phi, \end{aligned} \tag{8}$$

where θ, ϕ are the polar angles of the radius vector $\mathbf{r}$ measured from the nucleus in question.

Using (5), (6) and (8) in (7) and carrying out a considerable amount of simplification, we finally obtain

$$\begin{aligned} q_{xx} = {} & \frac{32\pi}{\Omega} \sum_{\mathbf{k}} \omega_{\mathbf{k}} \sum_{t} \sum_{\mathbf{K}>\mathbf{K}'} C_t(\mathbf{k},\mathbf{K}) C_t(\mathbf{k},\mathbf{K}') S(\mathbf{K}-\mathbf{K}') D(|\mathbf{K}'-\mathbf{K}|) \\ & \times \left\{ \left(\frac{6\pi}{5}\right)^{1/2} (Y_{22}(\mathbf{K}'-\mathbf{K}) + Y_{22}^*(\mathbf{K}'-\mathbf{K})) - \left(\frac{4\pi}{5}\right)^{1/2} Y_{20}(\mathbf{K}'-\mathbf{K}) \right\} \\ & - \frac{64\pi^2}{\Omega} \sum_{\mathbf{k}} \omega_{\mathbf{k}} \sum_{t} \sum_{\mathbf{K},\mathbf{K}'} \sum_{n_1 l_1 m_1} \sum_{n_2 l_2 m_2} C_t(\mathbf{k},\mathbf{K}) C_t(\mathbf{k},\mathbf{K}') (i)^{l_2 - l_1} \\ & \times Y_{l_1 m_1}(\mathbf{k}+\mathbf{K})\, Y_{l_2 m_2}^*(\mathbf{k}+\mathbf{K}') I(|\mathbf{k}+\mathbf{K}|, n_1 l_1) I(|\mathbf{k}+\mathbf{K}'|, n_2 l_2) \\ & \times S(\mathbf{K}) S(\mathbf{K}') F(n_1 l_1, n_2 l_2) \left\{ \left(\frac{6\pi}{5}\right)^{1/2} (\langle l_1 m_1 | 22 | l_2 m_2 \rangle \right. \\ & \left. + \langle l_1 m_1 | 2-2 | l_2 m_2 \rangle) - \left(\frac{4\pi}{5}\right)^{1/2} \langle l_1 m_1 | 20 | l_2 m_2 \rangle \right\} \\ & + \frac{128\pi^2}{\Omega} \mathrm{Re} \left(\sum_{\mathbf{k}} \omega_{\mathbf{k}} \sum_{t} \sum_{\mathbf{K},\mathbf{K}'} C_t(\mathbf{k},\mathbf{K}) C_t(\mathbf{k},\mathbf{K}') \sum_{n_1 l_1 m_1} (i)^{l_1} \right. \\ & \times Y_{l_1 m_1}^*(\mathbf{k}+\mathbf{K}') I(|\mathbf{k}+\mathbf{K}'|, n_1 l_1) S(\mathbf{K}) S(\mathbf{K}') \sum_{l' m'} (-i)^{l'} \\ & \times Y_{l' m'}(\mathbf{k}+\mathbf{K}) H(n_1 l_1, l', |\mathbf{k}+\mathbf{K}|) \left\{ \left(\frac{6\pi}{5}\right)^{1/2} (\langle l' m' | 22 | l_1 m_1 \rangle \right. \\ & \left. \left. + \langle l' m' | 2-2 | l_1 m_1 \rangle) - \left(\frac{4\pi}{5}\right)^{1/2} \langle l' m' | 20 | l_1 m_1 \rangle \right\} \right). \end{aligned} \tag{9}$$

$$q_{zz} = \frac{32\pi}{\Omega}\sum_{\mathbf{k}}\omega_{\mathbf{k}}\sum_{t}\sum_{\mathbf{K}>\mathbf{K}'}C_t(\mathbf{k},\mathbf{K})C_t(\mathbf{k},\mathbf{K}')S(\mathbf{K}-\mathbf{K}')D(|\mathbf{K}'-\mathbf{K}|)\left(\frac{16\pi}{5}\right)^{1/2}$$
$$\times Y_{20}(\mathbf{K}'-\mathbf{K}) - \frac{64\pi^2}{\Omega}\sum_{\mathbf{k}}\omega_{\mathbf{k}}\sum_{t}\sum_{\mathbf{K},\mathbf{K}'}\sum_{n_1l_1m_1}\sum_{n_2l_2m_2}C_t(\mathbf{k},\mathbf{K})C_t(\mathbf{k},\mathbf{K}')(i)^{l_2-l_1}$$
$$\times Y_{l_1m_1}(\mathbf{k}+\mathbf{K})\,Y^*_{l_2m_2}(\mathbf{k}+\mathbf{K}')I(|\mathbf{k}+\mathbf{K}|,n_1l_1)I(|\mathbf{k}+\mathbf{K}'|,n_2l_2)$$
$$\times S(\mathbf{K})S(\mathbf{K}')F(n_1l_1,n_2l_2)\left(\frac{16\pi}{5}\right)^{1/2}\langle l_1m_1|20|l_2m_2\rangle$$
$$+\frac{128\pi^2}{\Omega}\mathrm{Re}\Bigg(\sum_{\mathbf{k}}\omega_{\mathbf{k}}\sum_{t}\sum_{\mathbf{K},\mathbf{K}'}C_t(\mathbf{k},\mathbf{K})C_t(\mathbf{k},\mathbf{K}')S(\mathbf{K})S(\mathbf{K}')$$
$$\sum_{n_1l_1m_1}(i)^{l_1}Y^*_{l_1m_1}(\mathbf{k}+\mathbf{K})I(|\mathbf{k}+\mathbf{K}'|,n_1l_1)\sum_{l'm'}(-i)^{l'}Y_{l'm'}(\mathbf{k}+\mathbf{K})$$
$$\times H(n_1l_1,l',|\mathbf{k}+\mathbf{K}|)\left(\frac{16\pi}{5}\right)^{1/2}\langle l'm'|20|l_1m_1\rangle\Bigg), \tag{10}$$

and

$$q_{xz} = -\frac{32\pi}{\Omega}\sum_{\mathbf{k}}\omega_{\mathbf{k}}\sum_{t}\sum_{\mathbf{K}>\mathbf{K}'}C_t(\mathbf{k},\mathbf{K})C_t(\mathbf{k},\mathbf{K}')S(\mathbf{K}-\mathbf{K}')D(|\mathbf{K}'-\mathbf{K}|)$$
$$\times\left(\frac{6\pi}{5}\right)^{1/2}\{Y_{21}(\mathbf{K}'-\mathbf{K})+Y^*_{21}(\mathbf{K}'-\mathbf{K})\}$$
$$-\frac{64\pi^2}{\Omega}\sum_{\mathbf{k}}\omega_{\mathbf{k}}\sum_{t}\sum_{\mathbf{K},\mathbf{K}'}C_t(\mathbf{k},\mathbf{K})C_t(\mathbf{k},\mathbf{K}')S(\mathbf{K})S(\mathbf{K}')\sum_{n_1l_1m_1}\sum_{n_2l_2m_2}(i)^{l_2-l_1}$$
$$\times Y_{l_1m_1}(\mathbf{k}+\mathbf{K})\,Y^*_{l_2m_2}(\mathbf{k}+\mathbf{K}')F(n_1l_1,n_2l_2)I(|\mathbf{k}+\mathbf{K}|,n_1l_1)$$
$$I(|\mathbf{k}+\mathbf{K}'|,n_2l_2)$$
$$\times\left\{-\left(\frac{6\pi}{5}\right)^{1/2}(\langle l_1m_1|21|l_2m_2\rangle-\langle l_1m_1|2-1|l_2m_2\rangle)\right\}$$
$$-\frac{128\pi^2}{\Omega}\mathrm{Re}\Bigg(\sum_{\mathbf{k}}\omega_{\mathbf{k}}\sum_{t}\sum_{\mathbf{K},\mathbf{K}'}C_t(\mathbf{k},\mathbf{K})C_t(\mathbf{k},\mathbf{K}')S(\mathbf{K})S(\mathbf{K}')$$
$$\times\sum_{n_1l_1m_1}(i)^{l_1}Y^*_{l_1m_1}(\mathbf{k}+\mathbf{K}')I(|\mathbf{k}+\mathbf{K}'|,n_1l_1)\sum_{l'm'}(-i)^{l'}Y_{l'm'}(\mathbf{k}+\mathbf{K})$$
$$\times H(n_1l_1,l',|\mathbf{k}+\mathbf{K}|)\left(\frac{6\pi}{5}\right)^{1/2}\{\langle l'm'|21|l_1m_1\rangle+\langle l_1m_1|21|l'm'\rangle\}\Bigg). \tag{11}$$

where

$$D(|\mathbf{K}'-\mathbf{K}|) = \int_0^\infty j_2(|\mathbf{K}'-\mathbf{K}|r)\frac{\{1-\gamma(r)\}}{r}\,\mathrm{d}r, \tag{12}$$

$$I(|\mathbf{k}+\mathbf{K}|,nl) = \int_0^\infty P_{nl}(r)j_l(|\mathbf{k}+\mathbf{K}|r)r\,\mathrm{d}r, \tag{13}$$

$$F(n_1l_1,n_2l_2) = \int_0^\infty P_{n_1l_1}(r)P_{n_2l_2}(r)\frac{\{1-\gamma(r)\}}{r^3}\,\mathrm{d}r, \tag{14}$$

$$H\{n_1 l_1, l', |\mathbf{k}+\mathbf{K}|) = \int_0^\infty P_{n_1 l_1}(r) j_{l'}(|\mathbf{k}+\mathbf{K}|r) \frac{\{1-\gamma(r)\}}{r^2} \mathrm{d}r, \tag{15}$$

and

$$\langle l_1 m_1 | l_2 m_2 | l_3 m_3 \rangle = \int Y^*_{l_1 m_1}(\hat{r})\, Y_{l_2 m_2}(\hat{r})\, Y_{l_3 m_3}(\hat{r}) \sin\theta \mathrm{d}\theta \mathrm{d}\phi \tag{16}$$

The **k**-sums in (9)–(11) are taken over the irreducible part of the *BZ*. The first, the second and the third **k**-sums in each of the equations (9)–(11) give respectively the contributions from the plane wave, tight binding and the hybrid (i.e. plane wave-tight binding and tight binding-plane wave) part of the integral in (7). The symbols $\omega_{\mathbf{k}}, t, S$ and i used in (9), (10) and (11) are respectively the weighting factor assigned to **k** point, the occupied band index, the structure factor and the imaginary number $\sqrt{-1}$. The functions Y_{lm}, j_l and P_{nl} are the standard spherical harmonics, the spherical Bessel function of order l and the radial part of the atomic core function respectively. The latter is normalized according to the relation,

$$\int_0^\infty P^2_{nl}(r)\mathrm{d}r = 1. \tag{17}$$

The quantum numbers specifying the atomic core states are denoted by n, l, and m. The integrals in (12)–(15) and (17) were evaluated using the standard 5-point numerical integration procedure after generating the corresponding integrands at 201 mesh points each, chosen in a logarithmic r scale,

$$r_n = r_1 \exp(-(n-1)h) \quad \text{with} \quad r_1 \simeq 0{\cdot}00097 \text{ au and } h = 0{\cdot}05 \text{ au}.$$

The farthest distance up to which the integrations were carried out has the value $r_{201} \simeq 21{\cdot}45618$ au.

The angular integrals in (16), whose values for allowed angular momentum quantum numbers are tabulated by Tinkham [15] were used directly.

3. Results and discussion

In constructing the band wave functions Ψ_n, the atomic core functions used in the present work are those of Clementi [16]. In order to carry out the **k**-sum in (9)–(11), 176 sample **k** points are suitably chosen in $\frac{1}{4}$th irreducible part of the *BZ*. For this purpose the wedge denoting the irreducible part of the *BZ* is divided into 176 volume elements, out of which 150 elements are parallelopipeds and the remaining 26 elements are triangular prisms. The **k**-vectors denoting the centroids of these elements are used as the representative points. To each **k** point so chosen, a weighting factor in proportion to the volume it represents is assigned. Thus, the effective number of **k** points chosen in the full *BZ* comes to 704. Energy and eigen functions are calculated at each of these 176 **k**-points. For this purpose the model wave function at each **k** point is expanded in 23 plane waves corresponding to the shortest 23 wave vectors, $|\mathbf{k}+\mathbf{K}|$ for that **k**-point. Thus, the size of the matrix diagonalized at each **k**-point is 23 x 23. With this choice, convergence of energy and eigen functions is good. The energies of the occupied bands have converged to within 0·001 Ryd. We wish to remark here that a choice of more representative **k** points than 176 in irreducible part of *BZ* would, in principle, give more accurate result. But the computation time as

well as the memory for storage of data increase many fold. From past experience as well as the the present calculation we have found that the accuracy of EFG with respect to variation in the number of **k** points is good to within 1% for the number of **k**-points choosen in the present work.

We have compared the results of the present band calculation with those of APW calculation [8]. Not only the shape of the bands but also the Fermi energy and the density of states $\mathcal{N}(E_F)$ agree quite well. While the Fermi energy E_F in the present calculation, measured from the bottom of the band as zero of energy scale, turns out to be 0·784 Ryd, it is 0·807 Ryd in APW calculation [8]. The density of states $\mathcal{N}(E_F)$ in the present calculation is found approximately $(0{\cdot}97 \pm 0{\cdot}01)\,\mathcal{N}_0(E_F)$, where $\mathcal{N}_0(E_F)$ is the free-electron value. This compares well with the value of $(0{\cdot}96 \pm 0{\cdot}04)\,\mathcal{N}_0(E_F)$ obtained in APW calculation [8]. It also agrees reasonably well with density of states, $\mathcal{N}(E_F) = (0{\cdot}92 \pm 0{\cdot}09)\,\mathcal{N}_0(E_F)$ deduced indirectly [8] from the measured values of the electron specific heat. In arriving at the measured value for the density of states, the effect of electron-phonon interaction has been duly taken into consideration [8]. The value of electron-phonon enchancement factor used [8] for this purpose is $\lambda = 0{\cdot}63$.

There is however a minor discrepancy between the two calculations with regard to the filling of the fifth band. While in the APW calculation [8], the fifth band is vacant, in the present work, there is a small electron pocket in this band. The other band calculation in β-Ga is by Hunderi [7]. However, he had used the same form factor [12] as used in the present work but with a less number of basis functions and an approximate β equal to 90°. The details of E_F and $\mathcal{N}(E_F)$ are however not available in ref. [7] for comparison with the present work.

Next we discuss the results of field gradients. Since the values of $\gamma(r)$ for β-Ga in solid state are not available, the integral in (12), (14) and (15) have been evaluated by assuming $\gamma(r) = 0$. This assumption would lead to a negligible error in the contribution to EFG arising from the tight binding part of the band wave functions. This is so because in the region (see integrals (14) and (15)) where the amplitude of the tight-binding function is large, $\gamma(r)$ is small and where $\gamma(r)$ is large the amplitude of atomic wave function is negligible. The plane wave (PW) contribution, on the other hand, is likely to be significantly affected on account of the relatively long range nature of plane wave states (see integral (12)) and the saturation value of $\gamma(r)$ at large r. In the absence of solid state $\gamma(r)$, we have estimated the shielding for the PW contribution as follows. The shielded PW contribution to q_{xx}, q_{zz} and q_{xz} are calculated using the available [17] free-ion $\gamma(r)$. From these the ratios of the shielded to the corresponding unshielded ($r(r) = 0$) PW contributions are obtained. These are found to be approximately 1·76, 1·96 and 0·55 for q_{xx}, q_{zz} and q_{xz} respectively. To get the corresponding numbers in the solid state, that is, the ratios of the shielded plane wave contributions using solid-state $(1 - \gamma(r))$ to the corresponding unshielded PW contributions, we have used the approximation,

$$\{1-\gamma(r)\}_{\text{solid}} \approx \{1-\gamma(r)\}_{\text{free-ion}} \frac{(1-\gamma_\infty)_{\text{solid}}}{(1-\gamma_\infty)_{\text{free-ion}}} \tag{18}$$

and used this in the integral (12) to obtain the shielded PW contribution in solid state. This approximation is very good at large distance where $\gamma(r)$ is nearly a constant equal to the value of γ_∞ for the respective system. From this approximation, it is easy to see that the shielding factors, that is, the ratios of the shielded PW contribution

using solid state $(1-\gamma(r))$ to the unshielded PW contribution are approximately equal to the product of $(1-\gamma_\infty)_{\text{solid}}/(1-\gamma_\infty)_{\text{free-ion}}$ and the corresponding shielding factors obtained using free-ion $(1-\gamma(r))$.

The ionic contributions to EFG, as previously stated, are taken from the work of Lodge [6] with the following modifications. The cartesian axes chosen in the present work are different from those of Lodge [6] who had taken x and z axes parallel to **c** and **b** axes respectively. Therefore his results needed to be transformed to our coordinate system. Secondly, the free-ion value of the antishielding factor γ_∞ used by Lodge [6] was replaced by the value of γ_∞ appropriate to the solid state. The latter taken from the work of Schmidt *et al* [18] is equal to $-16{\cdot}986$.

We wish to remark here that in evaluating the ionic contribution the point-ion approximation has been used for all the distant ions than the one at whose site EFG is required. This is a reasonably good approximation considering 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 however been included through the Sternheimer antishielding factor. But the contribution to EFG due to the induced multipoles of the deformed cores of the distant ions, which is expected to be small has been neglected.

The components of EFG tensor in the chosen axes system arising from the lattice ions as well as the band electrons are listed in table 1. The net EFG tensor is diagonalized and the principal components q_{XX}, q_{YY} and q_{ZZ} are identified according to the criterion,

$$|q_{XX}| \leqslant |q_{YY}| \leqslant |q_{ZZ}|. \tag{19}$$

The asymmetry parameter is calculated using the relation,

$$\eta = \frac{q_{XX} - q_{YY}}{q_{ZZ}} \tag{20}$$

The pure quadrupole resonance frequency is related [2] to q_{ZZ} and η by

$$\nu = \frac{e^2 q_{ZZ} Q}{2h}\left(1+\frac{\eta^2}{3}\right)^{1/2} \tag{21}$$

where e, h and Q are respectively the charge on electron, Planck's constant and the quadrupole moment of the nucleus in question. For the isotope ^{69}Ga, $Q = 0{\cdot}168$ barns [6].

Each component of electronic EFG tensor in table 1 consists of a sum of contributions from a pure plane wave part and a non-plane wave part of the band wave function Ψ_n. As discussed in ref. [13], the non-plane wave part has been further split into a sum of $s-d$, $p-p$, $d-d$ type terms depending on the angular momentum of tight-binding states involved in these contributions and a 'distant' term arising from the $l=0$ component of the charge distribution on all the other lattice sites than the one in question. The PW and the none plane wave type contributions are summarized in table 2. It may be noted from this table that for each component of EFG, the $p-p$ term has the largest magnitude. This is understandable because, the p-orbitals give rise to the most asymmetric charge distribution. Now coming back to table 1, one notices that between the two diagonal components q_{xx} and q_{zz} of the

Table 1. Components of EFG tensor in crystal axes system. All the EFG's are expressed in atomic units.

Contribution	q_{xx}	q_{zz}	q_{xz}
Electronic	−0·29488	0·16284	0·00289
Ionic	0·04478	−0·12373	0·00786
Total	−0·25010	0·03911	0·01075

Table 2. Electronic contibution to various components of EFG tensor in β-Ga. All the EFG's are expressed in atomic units.

	PW	$s-d$	$p-p$	$d-d$	dist.	total
q_{xx}	−0·01789	−0·00540	−0·26444	−0·00792	0·00082	−0·29488
q_{zz}	0·05615	−0·00002	0·10261	0·00635	−0·00225	0·16284
q_{xz}	−0·00097	0·00045	0·00292	0·00035	0·00014	0·00289

Table 3. Net EFG, asymmetry parameter and pure quadrupole resonance frequency in β-Ga at 248 K. The EFGs are expressed in atomic units and the resonance frequency in MHz.

Theory			Expt.[a]		
q	η	ν	$\lvert q\rvert$	η	$\lvert\nu\rvert$
−0·250	0·684	−5·318	0·247	0·305	4·952

[a]These data are taken from [2] after interpolation.

electronic contribution, the former is larger in magnitude than the latter. This suggests that the electron distribution around x-axis is more compact and localized than in the yz plane. The ionic contributions, on the other hand, show an opposite trend.

Table 3 summarizes the experimental [2] and the theoretical results for the field gradient, asymmetry parameter and the resonance frequency at 248 K. The experimental data listed are the results of interpolation made from the temperature dependent data given in ref. [2]. The experimental EFG has been deduced by using the prue quadrupole resonance frequency and the asymmetry parameter in (21).

A comparison of data in table 3 shows that the magnitudes of the calculated quadrupole resonance frequency and the net EFG agree with experiment to within 7% and 2% respectively. There is however discrepancy with respect to the sign of the EFG and the magnitude of η. While theory gives negative sign, experiment [3] predicts a positive sign for the net EFG. The latter prediction is based on the quadrupole anomaly data [3] and the sign of the anisotropic Knight shift in β-Ga [2]. We offer the following plausible explanations for the said discrepancy.

In order to see whether the approximate shielding factor used in the present work for the PW contribution could be responsible for the discrepancy, we have calculated the net EFG q and η for three sets of progressively increasing shielding factors. The results are summarized in table 4. In this table the first row refers to free-ion shielding

Table 4. Variation in the EFG and asymmetry parameter with the change in the shielding factors of the *xx*, *zz* and *xz* components of the plane wave contribution. The EFGs are expressed in atomic units.

Components			q	η
xx	*zz*	*xz*		
1·76	1·96	0·55	−0·244	0·842
2·75	3·07	0·85	−0·250	0·684
5·28	5·88	1·62	−0·267	0·319

factor, the second row gives the shielding factors used in the present work and are obtained by multiplying the corresponding free-ion shielding factors by the ratio $(1-\gamma_\infty)_{\text{solid}}/(1-\gamma_\infty)_{\text{free-ion}}$. The third row lists a set of shielding factors which give η and the magnitude of q very close to the corresponding experimental values. It may be noted that in all these cases, in spite of variation in shielding factors, the sign of the net EFG is negative with negligible variation in magnitudes. The asymmetry parameter, on the other hand, varies appreciably. So we conclude that any uncertainty in the PW shielding factor may not account for the sign reversal of the net EFG. On the other hand, there are reasons to believe that this discrepancy may owe its origin to the theoretical value of quadrupole anomaly [4] and the experimental value of anisotropic Knight shift [2], both of which were used in predicting the sign of the experimental EFG as positive.

As to the quadrupole anomaly, eq. (12) of Pyykkö [4] which has been used in obtaining the expression for the pseudo quadrupole contribution does not hold for β-Ga since the latter does not have a three fold or higher rotational symmetry axis, a condition for the validity of the said equation. Secondly and more importantly, the experimental [2] deduction of anisotropic Knight shift K' from the relation, $K(\theta) = K_{\text{iso}} + \frac{1}{2}K'\,(3\cos^2\theta - 1)$ may be erroneous in β-Ga as the latter is neither axially symmetric nor the principal axis of its Knight shift tensor is coincident with q_{zz}, the two requirements for the validity of the above relation. Hence the sign of K' determined in experiment [2] may not be reliable and therefore all subsequent analysis using K' for the prediction of the sign of EFG may fall apart. In order to settle the discrepancy in the sign of the EFG, it is therefore suggested that more direct measurement of the sign than deducing it from the quadrupole anomaly data be performed. The procedure of time-differential-perturbed-angular-correlation (TDPAC) involving β-γ correlation [19] and the one that uses Mössbauer spectroscopy (MS) [20] may be used for the direct measurement of the sign of the EFG.

It is hoped that the shielding factors in the third row of table 4, which give better values of q and η may result if the values of $\gamma(r)$ appropriate to the solid state are used in the calculation of EFG.

4. Conclusion

In conclusion, we state that the model potential calculation gives the magnitude of EFG and the quadrupole resonance frequency in β-Ga in good agreement with experiment. The results, particularly the asymmetry parameter are expected to

improve, if the values of $\gamma(r)$ appropriate to solid state are used. For settling the existing discrepancy in the sign of the EFG, it is suggested that more direct measurement of the sign as accomplished in TDPAC or MS be performed rather than deducing it from the quadrupole anomaly data.

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