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M A Ball† and G P Srivastava‡

† Department of Applied Mathematics and Theoretical Physics, PO Box 147, The University of Liverpool, Liverpool L69 3BX, UK
‡ Semiconductor Physics Group, Department of Physics, University of Exeter, Exeter EX4 4QL, UK

Abstract. Using a method derived in a previous paper, information at $g = 0$ about the pseudoatoms in the polar semiconductor GaAs is obtained from total-energy calculations. The latter were carried out using the Kohn–Sham equations within the local density approximation. We briefly review the method and the difficulties, particularly over the charges, of applying it to polar semiconductors. The linear dependence of the equations for the parts of the pseudoatoms at any given reciprocal lattice vector g is shown to arise because first-order terms can only have three independent equations whereas point group symmetry in general gives rise to four equations. The results suggest that the rigid ions are well-localized and well-behaved functions of position. Contour plots of the charge densities in the [110]–[001] plane are drawn. They show that most of the changes take place around the As ion and at the bond charges. The deformation takes place mainly at the bond charges and shows a charge transfer between the bond charges themselves; it also smooths out, very slightly, effects caused by the movement of the rigid ions.

1. Introduction

The change in the electronic charge density to first order in the ionic displacements when a phonon is present in a crystal is an important quantity (Ball and Srivastava 1992, hereafter referred to as I). It can be described in terms of density response functions, and in a more physical way in terms of pseudoatoms (Ball 1975) or their near equivalent, quasi-ions (Falter 1988).

In I we described how to get information about the pseudoatom from total-energy calculations (TECs) in non-polar semiconductors such as germanium (Ge). In this paper we aim to do the same for the polar semiconductor gallium arsenide (GaAs), and to compare the results with those for Ge. In any material the change in the electronic charge density caused by a phonon of wavevector q can be written

$$(1/\tau) \sum_s \sum_g \delta R_s \cdot f_s(q + g) \exp(-\mathrm{i} g \cdot R_s) \exp(\mathrm{i}(q + g) \cdot r) \qquad (1)$$

where τ is the volume of the unit cell, δR_s is the displacement of the ion at R_s in the unit cell and g is a reciprocal lattice vector. $f_s(k)$ is a vector field which we shall call the displacement field for ions of type s.

In a polar semiconductor it is convenient to write (Ball 1977)

$$f_s(q + g) = f_{sc}(q + g) + f_{su}(q + g) \qquad (2)$$

where the first term takes into account the effects of the effective charges Z_s^{eff}:

$$f_{sc}(q + g) = -i\chi(q + g, q)q \cdot Z_s^{\text{eff}}\delta R_s \nu(q) \tag{3}$$

where χ is the electron density response function and $\nu(q)$ is the Coulomb potential. The second term in (2) can be written

$$f_{su}(q + g) = -i[(q + g)\rho_s(q + g) + b_s(q + g)] \tag{4}\dagger$$

which defines the pseudoatom, with ρ being the rigid ion part and b being the deformation: $b(k)$ is perpendicular to k. The way we have split $f_s(q + g)$ into the two parts, f_{sc} and f_{su}, has two consequences: the electronic pseudoatom, when taken in conjunction with its associated ion, is neutral, and its charge density is an analytic function. It is possible to split $f_s(q + g)$ in different ways, for example by incorporating part of $f_{sc}(q)$ into $f_{su}(q)$, and thus have a charged pseudoatom-plus-ion but then care must be taken to ensure the analyticity of the resulting $f_{su}(q + g)$ so that the resulting pseudoatom can be transformed into a real space function.

As in I, we shall be using TECs to derive the Fourier components of the electronic charge density. Our aim is to learn about all the terms in the displacement field $q = 0$. This requires knowledge of the effects of both longitudinal and transverse phonons. Unfortunately as yet it has only been possible to calculate the changes in charge density due to transverse phonons; because of the long-range Coulombic effects, calculation of the effect of longitudinal phonons in GaAs has not yet proved possible. This means that we are only able to calculate the pseudoatom, i.e. $f_{su}(g)$, as $f_{sc}(g)$ is zero for transverse phonons. The results are nevertheless of interest as they reveal similarities and differences between GaAs and Ge.

2. Procedure

Our aim then is to calculate $\rho^G(g), \rho^A(g), b^G(g), b^A(g)\ddagger$ using the Fourier components of the electronic charge density from TECs. These calculations were made for the unperturbed crystal and for the crystal with a $q = 0$ transverse phonon. For the distorted crystal we considered displacements in the [111] direction, as in I, with $\delta R^G = \pm0.005a(1, 1, 1), \pm0.01a(1, 1, 1)$ and $\delta R^A = \mp0.005a(1, 1, 1), \mp0.01a(1, 1, 1)$, a being the cubic lattice constant of GaAs.

The procedure outlined in I was used to eliminate, to an acceptable approximation, the anharmonic effects from the TEC results.

As there is no inversion symmetry in GaAs, there is no particularly convenient place for the origin of the unit cell. The position of this origin however has no effect on the Fourier components of the pseudoatoms as these always take their origin at their own ion.

The pseudoatom have both real and imaginary parts. The TECs, after the anharmonic effects have been removed, give the real and imaginary parts of

$$(-i/\tau) \sum_\alpha \delta R_\alpha^G \{[g_\alpha \rho^G(g) + b_\alpha^G(g)] \exp(-ig \cdot R^G)$$

$$+ \delta R_\alpha^A [g_\alpha \rho^A(g) + b_\alpha^A(g)] \exp(-ig \cdot R^A)\} \tag{5}$$

† Please note that the factor $-i$ was missing in equation (2) of I.

‡ The superscripts refer to the different types of ion: G for gallium and A for arsenic.

where the subscript α stands for the x, y or z component.

Translational symmetry (Ball 1975) requires

$$b_\alpha^G(g) \exp(-i g \cdot R^G) + b_\alpha^A(g) \exp(-i g \cdot R^A) = 0 \qquad (6)$$

so that the magnitude of the two pseudoatoms' deformations (at $q = 0$) are equal, and half the magnitude of the total deformation for these displacements.

Point group symmetry is also important. As we pointed out in I, point group symmetry ensures that, for a general value of g, e.g. $(2\pi/a)[5, 3, 1]$, the terms (5) for either the real or imaginary parts fall into four sets. Applying equation (15) of I, we see that only three of these can be independent, because δR has only three independent components. Thus the four sets are linearly dependent, as is borne out approximately by the TEC results. To ensure exact obedience to this linear dependence requirement, we modified the TEC results in the way described in I.

We thus obtain, for a general value of g like the above, three equations from the TECs of the distorted crystal and one equation from the perfect crystal, for each of the real and imaginary parts. There are also the two (real and imaginary) orthogonality equations for the deformation. There are sixteen unknowns, four for the rigid ions and twelve for the deformation. Six of the latter can be replaced because of the translational invariance condition (6). Thus the number of simultaneous equations equals the number of unknowns.

3. The total-energy calculations

In order to calculate the total energy of undistorted and distorted GaAs we used a plane-wave pseudopotential method within the local density approximation (Hohenberg and Kohn 1964, Kohn and Sham 1965). Norm-conserving pseudopotentials for Ga^{3+} and As^{5+} ions were taken from Bachelet *et al* (1982). Within the local density approximation, the many-body electron–electron exchange and correlation interactions were considered by using the scheme of Ceperley and Alder (1980), as parametrized by Perdew and Zunger (1981). Well-converged self-consistent solutions to the Kohn–Sham equations were obtained by truncating the plane-wave set for the pseudowavefunction expansion at the kinetic energy cut-off, 18 Ryd.

For the undistorted GaAs crystal the Brillouin zone summation, required for a self-consistent solution of the Kohn–Sham equations, was performed by using two special k points within the irreducible segment of the zone (Chadi and Cohen 1973). Total energy results for six different cell volumes were fitted to the Murnaghan equation of state (Murnaghan 1944). The resulting equilibrium lattice constant, bulk modulus and pressure derivative of the bulk modulus were determined to be $a = 5.531$ (5.653) Å, $B_0 = 0.730$ (0.747) Mbar, and $B_0' = 4.34$ (4.67), in good agreement with other *ab initio* theoretical calculations (Kunc and Martin 1981, Froyen and Cohen 1983) and with experimentally measured results (given in parentheses) (*Landolt–Börnstein* 1982). The Kohn–Sham equations were once again solved self-consistently at the equilibrium lattice constant and the electronic charge density coefficients thus calculated.

As mentioned in section 2, for the TO(Γ) mode of atomic vibrations the basis atom Ga and As were displaced along [111], thus either stretching the Ga–As bond or compressing it. Such a distortion leaves the translational symmetry of the crystal unaltered, but reduces the point group symmetry from T_d to C_{3v}. For this reduced symmetry the Brillouin zone summation was performed by using a set of five special k points (Yin and Cohen 1982).

For the distorted crystal, the total energy and the electronic charge density coefficients were once again calculated at the equilibrium lattice constant.

Writing $E(\delta R)$ as the harmonic part of the total energy of the crystal with the atomic displacements mentioned above, the frequency of the 'frozen phonon' in the $\mathrm{TO}(\Gamma)$ mode was obtained from the relation

$$\omega^2[M^G(\delta R) + M^A(\delta R)]/2 = E(\delta R \neq 0) - E(\delta R = 0). \tag{7}$$

Our calculated value of $\nu = \omega/2\pi$ is 8.28 THz, which agrees extremely well with the theoretical value reported earlier (Kunc and Martin 1981, Kunc 1985) and is within about 1% of the low-temperature experimental measurement of 8.19 THz (Dolling and Waugh 1965).

4. Results

The calculated values of the pseudoatom quantities are given in table 1†. We note that ρ_R^G and ρ_R^A are smooth decreasing functions of $\|g\|$, as is ρ_R^{Ge}. This suggests that it should be possible to construct a simple analytical model of the rigid ion in real space in these crystals. Moreover the model should be fairly well localized and because the imaginary parts of $\rho(g)$ are small, the rigid ions do not deviate from spherical symmetry by a large amount.

In figure 1 the electronic charge density in the $[\bar{1}\,1\,0]$ plane for the equilibrium lattice is shown. This clearly shows the extra charge around the As ion, while there is a diminution of charge in other regions and around the Ga ion. There are two signs of the existence of bond charges: firstly, the charge distribution around the As ion is elongated towards the Ga ion; secondly, as can be seen in figure 2, there is a lobe of maximum charge density along the Ga–As bond, shifted somewhat towards the As ion.
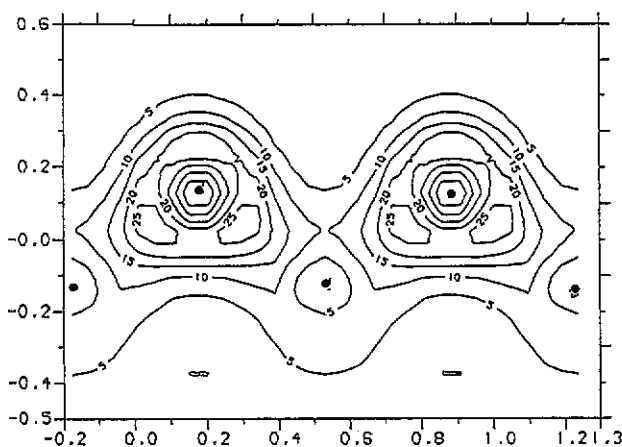
Figure 1. The electronic charge density in the $[\bar{1}\,1\,0]$ plane for the equilibrium lattice in GaAs. The units are electrons per unit cell volume. The Ga ion is at $-(1, 1, 1)/8$ and the As ion at $(1, 1, 1)/8$.

† There was an error in table 2 of I. The results for (3, 3, 1) should read:
$$-0.113\,64 \qquad -0.036\,57 \qquad -0.036\,36 \qquad -0.036\,36 \qquad 0.218\,14.$$
These results make $\rho(g)$ a smooth function of g, whereas previously there seemed to be an anomaly at (3, 3, 1) in Ge.

Table 1. Fourier components of the pseudoatom for Ga and As in GaAs. The results are in units of electronic charge, except those marked* which are in units of 10^{-2}. (Where there is no entry, the result is zero.)

g		$\rho^G(g)$	$\rho^A(g)$	b_x^G	b_y^G	b_z^G
(111)	Re	−0.664 49	−1.828 09	—	—	—
	Im	−0.037 95	0.123 55	—	—	—
(002)	Re	−0.443 48	−1.249 00	—	—	—
(022)	Re	0.037 72	−0.056 55	—	—	—
	Im	0.0	0.0	1.624 96	0.0	0.0
(113)	Re	0.130 09	0.188 04	0.383 03	0.383 03	−0.255 35
	Im	−0.032 82	0.077 94	0.663 33	0.663 33	−0.442 22
(222)	Re	0.136 40	0.203 08	—	—	—
	Im	−0.083 67	0.180 09	—	—	—
(004)	Re	0.137 06	0.267 00	—	—	—
(331)	Re	0.073 58	0.210 04	0.003 81	0.003 81	−0.022 84
	Im	0.027 27	0.044 71	−0.011 92	−0.011 92	0.071 53
(024)	Re	0.076 26	0.213 84	0.0	−0.346 34	0.173 17
	Im	0.0	0.0	0.059 82	0.0	0.0
(224)	Re	0.041 59	0.161 19	0.040 41	0.040 41	−0.040 41
	Im	−0.011 79	0.026 81	—	—	—
(333)	Re	0.027 94	0.130 01	—	—	—
	Im	−0.006 61	0.025 29	—	—	—
(115)	Re	0.036 89	0.138 84	−0.050 27	−0.050 27	0.020 11
	Im	0.000 39	0.005 74	−0.097 34	−0.097 34	0.038 94
(044)	Re	0.0	0.0	—	—	—
	Im	0.076 77	0.011 38	−0.174 14	0.0	0.0
(006)	Re	0.006 95	0.060 28	—	—	—
(135)	Re	0.005 49	0.059 84	0.075 41	−0.003 04	−0.013 26
	Im	0.000 98	0.002 48	−0.074 87	0.032 46	0.004 50
(442)	Re	0.005 43	0.054 00	−0.009 15	−0.009 15	0.036 60
	Im	0.001 15	0.006 25	0.002 16	0.002 16	−0.008 63
(026)	Re	0.004 67	0.027 70	0.0	0.033 11	−0.011 04
	Im	0.0	0.0	−0.100 33	0.0	0.0
(335)*	Re	−0.075 53	1.8392	−0.0712	−0.0712	0.080 5
	Im	0.166 83	0.258 37	−0.7847	−0.7847	0.941 6
(226)*	Re	−0.252 13	1.5142	1.3234	1.3234	−0.8823
	Im	0.211 71	−0.008 79	0.0474	0.0474	−0.0316
(444)*	Re	−0.281 77	0.255 27	—	—	—
	Im	−1.1731	1.4044	—	—	—
(551)*	Re	−0.367 55	−0.330 03	0.3039	0.3039	3.0394
	Im	0.068 03	−0.017 95	0.1827	0.1827	−1.8268
(117)*	Re	−0.433 73	−0.223 63	2.0823	2.0823	−0.5949
	Im	0.036 97	0.076 27	−1.2130	−1.2130	0.3466
(046)*	Re	−0.1480	−0.2008	0.0	0.9650	−0.6433
	Im	0.0	0.0	1.1113	0.0	0.0
(246)*	Re	−0.3304	−0.8272	0.2729	0.2721	−0.2724
	Im	−0.0036	−0.0141	2.9429	1.4890	−1.9736
(553)*	Re	−0.3382	−0.9694	−0.2890	−0.289 0	0.9633
	Im	0.0718	−0.1319	0.3029	0.3029	−1.0096
(731)*	Re	−0.2836	−0.9132	−2.1647	5.3363	0.8950
	Im	0.0387	−0.0040	−0.2551	0.6906	−0.2859

To try to understand the nature of the pseudoatoms, we have drawn some contour plots of various electronic charge densities. These plots are illustrative, and so only involve the results from the 15 smallest values of $\|g\|$. Checks were made to see that the resulting

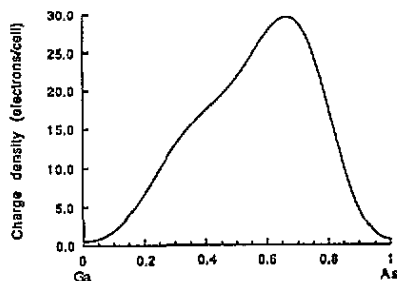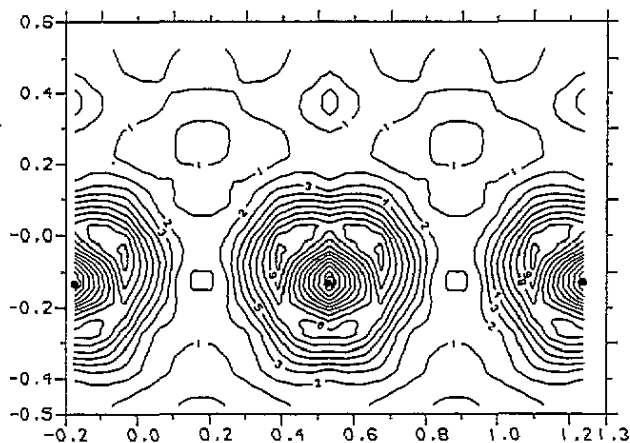**Figure 2.** Electronic charge density along the Ga–As bond length. The units are electrons per unit cell volume.

Figure 3. The electronic rigid ion for Ga. The units are electrons per unit cell volume.
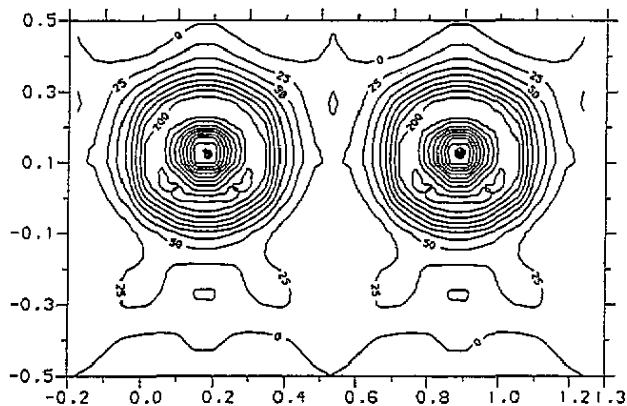

Figure 4. The electronic rigid ion for As. The units are 10^{-1} electrons per unit cell volume.

contour plots were qualitatively correct.

Figures 3, 4 and 5 show the rigid ions of the Ga, As and Ge pseudoatoms respectively, for pseudoatoms situated at points separated by a lattice vector. It should be remembered that the pseudoatom plus its associated ion is neutral in each case. Note that the pseudoatoms are concentrated around their own ions—i.e. there is almost no charge around the other ion in the cell. This shows that the rigid ions are localized. The contours also show that they are well-behaved entities. The effect of the bond charges is just about visible in all three cases. It is also clear that the electronic rigid ion for As is much larger than for Ga, and significantly larger than for Ge.
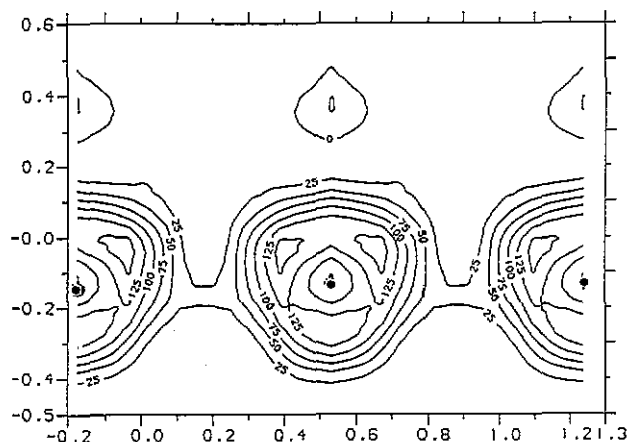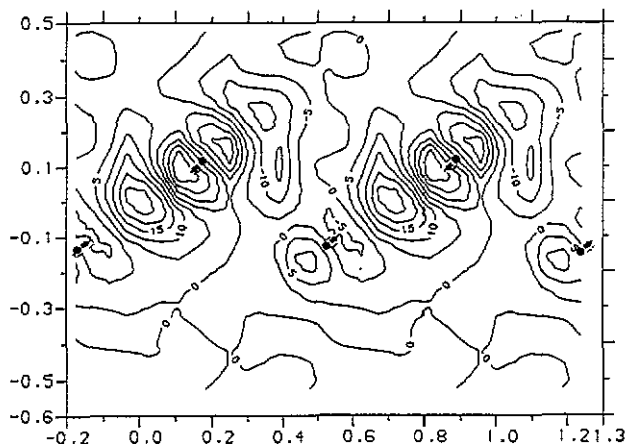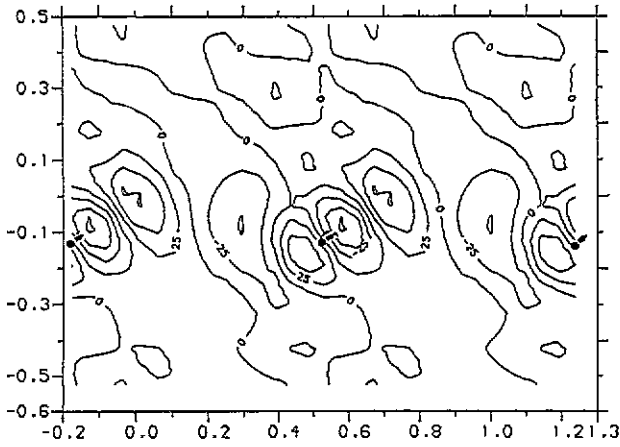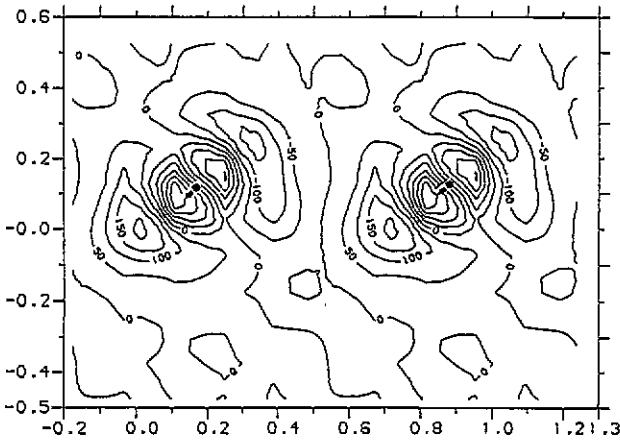
Figure 5. The electronic rigid ion for Ge (at $-(1, 1, 1)/8$). The units are 10^{-1} electrons per unit cell volume.

Figure 6. The total change in the electronic charge density when the Ga ion moves $(1, 1, 1)0.005a$ and the As ion moves $-(1, 1, 1)0.005a$. The units 10^{-2} electrons per unit cell volume.

Figure 6 demonstrates the first-order change in charge density when both ions move in such a way that a compression of the bond occurs. A comparison should be made with figure 4 of I, when the Ge ions move (causing a bond stretch, but as this is first order only, only a change in sign occurs). In GaAs there is an overall larger change in charge density with the changes occurring mainly on one ion (As) and the bond charge.

In figures 7, 8 and 9, the first-order changes in charge density when only the Ga, As and Ge ions, respectively, move are presented. The changes when the As ions move are a factor of seven times greater than the changes when the Ga ions move. An interesting feature of these three plots is that there is almost no effect at the non-moving ions. This means that any polarization effects are either non-existent or very small. This may not be surprising in Ge but is a surprise in the polar semiconductor.

Figures 10 and 11 show the first-order change in charge density due to the rigid ion and to the deformation part of the Ga pseudoatom respectively, when the Ga ion moves. Note that figure 7 is the sum of figures 10 and 11. We can see that the effect of the deformation is small in comparison with the effect of the rigid ion. Figure 11 should be compared with the similar plot for Ge (i.e. figure 5 of I. In that plot however both ions moved and in such a way that the bond stretched). In both cases the effects of the deformation are twofold: they are mainly concentrated at the bond charges with a small effect at the ions. The effect
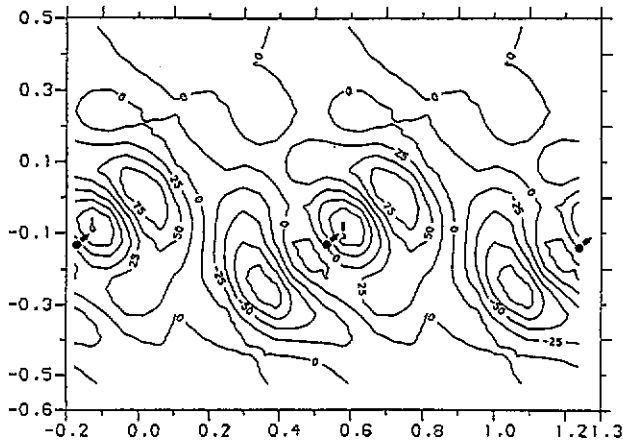
Figure 7. The change in the electronic charge density when the Ga ion moves (1, 1, 1)0.005a. The units are 10^{-2} electrons per unit cell volume.
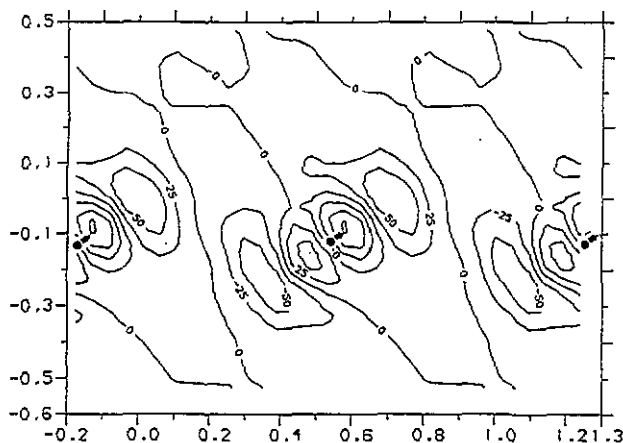

Figure 8. The change in the electronic charge density when the As ion moves $-(1, 1, 1)0.005a$. The units are 10^{-2} electrons per unit cell volume.
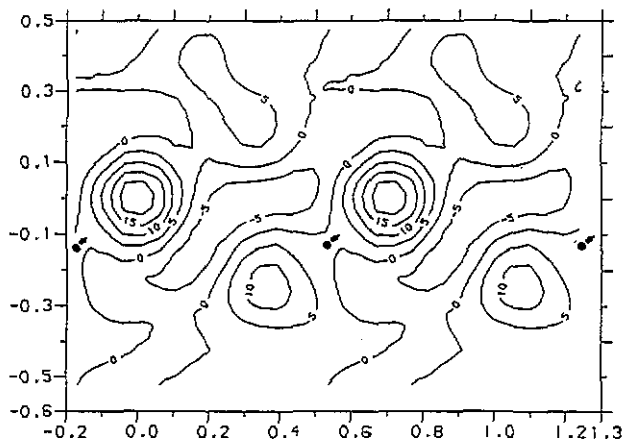

Figure 9. The change in the electronic charge density when the Ge ion moves (1, 1, 1)0.005a. The units are 10^{-2} electrons per unit cell volume.

at the bond charge is an increase in the total bond charge when the bond is compressed. As first-order effects are linear, there must be a decrease in the charge of the bond charge if the

Figure 10. The change in the electronic charge density due to the Ga rigid ion when the Ga ion moves $(1, 1, 1)0.005a$. The units are 10^{-2} electrons per unit cell volume.

bond length is increased. Simple arithmetic shows that the total decrease in the other bond charges around any particular ion exactly cancels the increase in the original bond charge; i.e. deformation causes charge transfer between the bond charges around an ion.

Figure 11. The change in the electronic charge density due to the deformation part of the Ga pseudoatom when the Ga ion moves $(1, 1, 1)0.005a$. The units are 10^{-2} electrons per unit cell volume.

The deformation at the ions look as if it smooths out the rigid movement of the rigid ion by a small amount.

The plots may be able to tell us something about the phenomenological models which have been used to explain the phonon spectra of Ge and GaAs. Our results suggest that a suitable model would include a localized rigid ion giving rise to short-range forces (probably only first-and second-nearest-neighbour forces) and charge transfer between the bond charges. Although it is unreasonable, even dangerous, to make deductions about phenomenological models for lattice dynamics on the basis of only the TO(Γ) calculations presented in this work, our finding of no perceptible polarization effects indicates that a bond-charge model, particularly if it incorporated charge transfer between the bond charges, would be more suitable than the shell model (Cochran 1959) which assumes the concept of polarizable ions. The better physical appeal of the bond-charge model was also established in a previous study of phonons in Ge (Srivastava and Kunc 1988). However we have not

been able to ascertain whether there is any non-rigid movement of the bond charges in GaAs as is required by the movable bond-charge model of Weber (1977).

To summarize, we have performed total energy calculations for the Fourier components of the charge density in GaAs for the unperturbed lattice and for the lattice perturbed by a transverse phonon at $g = 0$. From these we have calculated the pseudoatom components. The behaviour is similar to that in Ge except that there is more change at the As ion. We have established that deformation causes charge transfer between the bond charges around an ion and smooths out very slightly the movement of the rigid ion. The rigid ions are fairly well localized and reasonable functions of position.

Acknowledgment

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