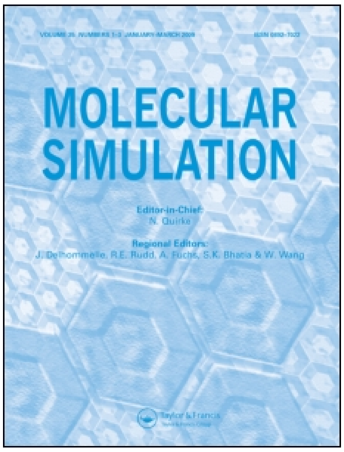

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Ab Initio Calculations of the Structure and Properties of Large Atomic Clusters

R. Jones[a]
[a] Department of Physics, University of Exeter, Exeter, UK

To cite this Article Jones, R.(1989) 'Ab Initio Calculations of the Structure and Properties of Large Atomic Clusters', Molecular Simulation, 4: 1, 113 — 120

To link to this Article: DOI: 10.1080/08927028908021968

URL: http://dx.doi.org/10.1080/08927028908021968

Molecular Simulation, 1989, Vol. 4, pp. 113–120
Reprints available directly from the publisher
Photocopying permitted by license only

AB INITIO CALCULATIONS OF THE STRUCTURE AND PROPERTIES OF LARGE ATOMIC CLUSTERS

R. JONES

Department of Physics, University of Exeter, Exeter, EX4 4QL, UK

(Received January 1989, accepted March 1989)

A discussion is given of the problems involved in computing the total energy, using local density functional methods, of a cluster of atoms with a real space basis set of Gaussian orbitals. Particular attention is given to the methods used to evaluate the Hartree and exhange-correlation energies and their potentials. Several applications are described: molecular structures and properties, the bond lengths and dynamic properties of bulk silicon and diamond, the local vibratory mode of carbon in silicon, and the structures of *H* and *H* related complexes in diamond and gallium arsenide.

KEY WORDS: *Ab Initio* Calculations, cluster methods, defects in solids

1. INTRODUCTION

Recently, there has been an explosion of calculations using local density functional theory (LDF) [1] with norm-conserving pseudopotentials [2] which have given spectacular results for structural and dynamic properties of solids exhibiting different types of bonding. A recent review is given by Ihm [3]. The success of the method can be attributed to the simplicity of the expression for the total energy. This is composed of the kinetic energy of valence electrons in occupied orbitals, a Hartree or electrostatic term, an exchange-correlation term, a electron pseudo-ion term and finally the ion-ion term. With the exception of the first, all the terms are explicitly functionals of the electron density n(r), and the actual total energy occurs for that density n(r) which minimises this energy expression subject to the total charge being fixed. This is to be contrasted with Hartree-Fock theory which minimises an energy expression which is a functional of a wave function dependent on the positions of all the electrons. Hence in that theory one must minimise an energy expression dependent on a function of a very large number of variables in contrast to the density functional approach.

Most LDF calculations for crystalline defects have used the plane wave supercell method [4,5] where the dominant computing step is the repeated diagonalisation of a very large complex matrix. Developments in molecular dynamical methods by Carr Parrinello aid this process [6,7,8]. One possible problem with the supercell method is that the effect of the interaction between defects in different unit cells may not be negligible. For example Van de Walle *et al.* [9] found for a 32 *Si* atom supercell containing a single *H* atom, the energy levels of *H* broadened into a band of width approximately 0.5 eV. Now since this band is half-filled we expect an interaction between *H* atoms in different unit cells to be asymptotically given by the Friedel expression:

$$\cos(2k_f r)/r^3$$

Such an interaction when summed over all cells varies weakly with cell size and rapidly with the position of the Fermi-level. Thus the interaction between H atoms in different cells may be significant even for a large supercell, and has a quite different value when the H atoms are moved from, say, a bond centred site to a tetrahedral interstitial site as such a move markedly changes the position of the H level, which is identical to the Fermi-level. This explains the very difficult results for the stable site of H in Si obtained by Chang and Chadi [10] who used an 8 Si atom supercell and Van der Walle *et al.* Another problem with this approach is that for some elements, eg O and F, the energy converges very slowly in the number of plane waves used. This is also true, of course, for transition elements. For these and other d-bonded materials, the LMTO method [11, 12] has been used. This method makes strong asumptions about the form of the potential which renders it appropriate for close-packed structures. Finally LCAO methods employing Gaussian bases have also been used for both covalent and d-bonded materials [13, 14]. For these calculations, the potential has often been fitted to a sum of Gaussians in order to carry out the evaluation of its matrix elements with respect to the Gaussian basis. Mednick and Lin [14] adopted a different scheme where the charge density was fitted to a linear sum of functions which were polynomials multiplied by Gaussians. These polynomials would be chosen so that Poisson's equation could easily be solved and thus the Hartree potential quickly evaluated. Matrix elements of the exchange-correlation potential would also be found by an expansion of the latter in the integrable functions.

At the same time that supercell methods have been developed, there has been rapid progress with Green function [15] and cluster methods [17–22]. The former are very expensive to implement and it is not easy to deal with complicated defects. For the latter, in the case of covalent materials , the uninteresting surfaces have been saturated with hydrogen atoms although embedding techniques are being introduced that obviate these [23,24,25]. For ionic solids the clusters have been surrounded by a large cluster of point charges. It is worth noting that the H saturated surface can cause problems. For example it is not easily possible to study graphite by looking at clusters of benzene and other cyclic compounds. The different electronegativities of C and H cause a charge transfer from H to C in benzene. This gives the molecule a quadrupolar moment and two benzene molecules will repel each other when they are parallel, as in the graphite structure, but attract when the molecular planes are orientated at 90 degrees to each other. Apparently benzene molecules do behave like this. Consequently it is difficult to describe the weak attraction between layers of graphite.

Here we concentrate on cluster methods using self-consistent norm-conserving pseudopotential theory. In particular we deal with the method introduced by us [22,26] and show how it enables the forces between atoms in a large cluster of up to 100 atoms to be evaluated. We shall illustrate the theory with several recent applications: molecular structures and properties, the structural and dynamic properties of diamond and silicon, the local vibrational mode of the carbon impurity in silicon, the remarkable structure of hydrogen in diamond, and the interaction of H with shallow impurities in gallium arsenide.

2. REAL SPACE CLUSTER METHODS

The central problem with a real space approach is the evaluation of the Hartree (or electrostatic) and exchange-correlation energies and their potentials. If there are N basis functions then the charge density is a bilinear sum of N^2 functions and the Hartree energy is a sum of N^4 integrals. It is impossible to evaluate all of these for a large cluster. The exchange-correlation energy is a non-linear function of the charge density again making it very difficult to evaluate. To make progress we rewrite the Hartree and exchange-correlation energies with expressions involving an approximate charge density $\tilde{n}(r)$. As $\tilde{n}(r)$ tends to $n(r)$ then these expressions approach the correct ones. Both of these expressions require about N^3 integrals to be found and, most importantly, both expressions can be differentiated to determine the Hartree and exchange-correlation potentials which are required when one uses the Euler-Lagrange equations to minimise the total energy. $\tilde{n}(r)$ is a fit to the correct charge density using a basis of Gaussian functions centred at atomic and bond centres. The coefficients of the fit, C_k, $k = 1,M$, are determined by minimising the error between our estimate of the Hartree energy and the exact expression. In this way our expression is a close *underestimate* of the Hartree energy but involves the computation of only $M\ N^2$ integrals where M is the number of fitting functions. This approach is not new [27], but we were the first workers to insist that this estimate of the Hartree energy replaces the true one in the density-functional expression for the total energy. If the fit to the charge density is constrained, eg by requiring the total fitted charge to be correctly given, then an extra (structurally dependent) term is introduced in the total energy which was not included by earlier workers [18, 27].

The exchange-correlation energy is a functional of the electron density and its evaluation proceeds by replacing the exact density by the fitted one. This reduces the problem to finding the average value of the exchange-correlation energy density under a single gaussian used in the fit. This can be analytically estimated using no more than three centre integrals and yields an expression for the exchange-correlation energy whose functional derivative can be found exactly. It should be noted that the replacement of the true charge density by the fitted one introduces errors which are most severe at the nuclei and the surface of the cluster. It is in these regions that the density is rapidly varying and the use of an exchange-correlation energy based on homogeneous electron gas theory most suspect. In the bonding region the charge density is larger and much less variable and the error we make in the exchange-correlation term much smaller.

The Euler-Lagrange equations give rise to a Shrodinger equation in which the potentials depend only on the fitting coefficients C_k. These are determined from the output charge density, so a self-consistent solution must be sought. We begin the process of finding the total energy by using as an input the coefficients $C_k(\text{in})$ to the fitted charge density arising from the superposition of atomic charge densities. Self-consistency can be achieved most rapidly by finding the fitting coefficients $C_k(\text{out})$ from the output charge density and using these to determine the next $C_k(\text{in})$. In fact the next set of input coefficients is then taken from a linear combination of up to three previous inputs with weightings determined by minimising the expected electrostatic energy difference between the output charge density and its input.

A crucial requirement for the optimisation of the structure of the atomic clusters is the rapid evaluation of the force on each atom. The Hellman-Feynman theorem gives this as the expectation of the gradient of the pseudopotential together with the gradient of the ion-ion interaction. Now if the bases functions depend on the structure which is the case when the centres of the Gaussians are located on atoms and bond-centres – then the gradient of the energy contains extra terms. It is however possible to group these terms so that the self-consistent charge density and not its gradient is required. Furthermore the analytic expression for the total energy can be easily differentiated to evaluate these terms. This of course means that force evaluation can be readily accomplished in reasonable CPU times.

The evaluation of frequencies of atomic vibrations requires a differentiation of these forces. Since there is no Hellman-Feynman expression for these second derivatives it is essential to compute the change in electron density which accompanies the movement of the atoms. This involves calculating the forces on the atoms when one is displaced by a small amount and then estimating the derivative numerically.

An important consideration is the size of the bases sets to be used. We often treat different parts of large clusters with different precision. So the electronic states on surface H atoms are described with a linear combination of 2 s- and similarly 2 p||-Gaussian orbitals with different exponents. Here p|| denotes a p-orbital parallel to the H bond. A single s- and p||- orbital are placed at bond centred sites, whereas atoms like Si, C, Ga and As are treated with a fixed linear combination of 4 to 6 s- and p-Gaussians. Central atoms and bond-centres are treated with a basis of 4 to 6 independent s- and p- Gaussians with different exponents. The basis for the charge density fit consists of 3 to 6 independent s-Gaussians at atomic sites and a single s-Gaussian at a bond centre. Generally we have found that structural and dynamic properties as well as total energy differences are unaffected by increasing the basis size but the total energy of the cluster invariably changes by an appreciable amount.

3. APPLICATIONS

3.1 Molecules [26]

It is essential to check that the theory we have described above yields accurate results for the simplest cases ie simple molecules. Bond lengths in water and the carbon dimer respectively are given within 2% of experiment. The HOH angle is also given within 1%. The vibration frequencies of the molecular vibrations are within 2% and the dipole moment within 1%. These results show that the approximations made in the method cause only small errors in the structure, dynamics and ground state charge density and we can have confidence in applying the method to larger clusters.
diamond and the carbon substitutional impurity in silicon [26, 28, 29].

3.2 Silicon, diamond and the carbon substitutional impurity in silicon [26, 28, 29]

The bond length of Si – Si can be found from the 15 atom molecule Si_5H_{12}. A complete optimisation gave a central Si – Si bond length of 2.313Å or 1.5% different from bulk Si. The cluster was then distorted and the resulting energies fitted to a simple Keating potential [30]. The bond-stretching term has a coefficient 3.323 eV/Å^2 and the bond bending one of .436 eV/Å^2. These are close to the Keating parameters fitted to zone boundary phonon frequencies by Baraff *et al.* [31] as well as the *ab-initio* calculations of Zur *et al.* [32]. When applied to a bulk solid they give a phonon spectrum to within 10% at zone-edges. The principal errors occur near the zone-edge because of the lack of longer ranged forces [33]. For the same reason, the elastic constants are poorly represented.

A similar approach can be used for diamond but as the surface atoms are now more charged than for the Si_5H_{12} cluster, a larger cluster must be used. The cluster $C_{11}H_{24}$ gives a C – C bond length within 1% of diamond. The double derivatives of the energy with respect to atoms out to the second shell can be used to determine the force-constants in a Musgrave-Pople potential [34]. This is the most general potential up to second order in bond length and bond angle variaitons. We found that we could not satifactorily fit these double derivatives to a Keating potential. This has only some of the second order terms, and neglects the correlation between bond stretch and bend. Using the Musgrave-Pople potential we found the phonon dispersion curves are given to within 10% at the zone edges.

This method is easily generalised to describe local vibratory modes of impurities. For example a cluster of CSi_4H_{12} gave a C-Si length of 1.897Å which is close to that observed in SiC (1.888Å). The bond stretching energy was fitted to a cubic and this potential together with a Keating one, for other bonds, was used with a relaxed 99 atom cluster CSi_{98}, to determine the structure and vibratory modes of the substitutional carbon impurity in silicon. The C – Si length now increase to 2.035Å and the triplet localised mode occurred at 684 cm^{-1}. This is 13% larger than the observed one [35] but our estimate is very sensitive to the C – Si length. A 4% increase in this reduces the frequency to within 5% of the observed values. It is clear that the structural and dynamic properties of bulk solids are largely determined by local bonding considerations. This is remarkable in that the individual terms which enter into the expression for total energy ie the one-electron energy, the electrostatic and exchange-correlation energies and the ion-ion energy, are properties of the whole cluster. There must be a subtle cancellation between these terms which allows bond lengths and force constants to be largely local properties.

3.3 Hydrogen in Diamond [36] and GaAs [37]

It is remarkable that the most stable position of interstitial *H* in diamond is at a bond-centred (BC) site and not a tetrahedral (T) interstitial one. This is due to the attraction of the proton to the bond charge. The electron bound to the proton lies in a state made up of antibonding $p\|$ -orbitals on the adjacent C atoms, and hence avoids the bond centre. There is direct evidence of this stable configuration from muon-spin rotation experiments [38]. We found that the C – H – C bond is increased by a massive 43%. These results agree with quantum chemical calculations [39, 40]. One would have also thought that molecular H would be stable in diamond [41]. Suprisingly our calculation carried out on a 56 atom cluster $C_{26}H_{30}$ including a pair of atoms showed that the stable H_2 defect is an association of bond-centred H with a H atom at an anti-bonding position. This is rather like a donor-acceptor pair: for the highest occupied level for H at a BC site is close to the conduction band edge (Ec) whereas it lies around mid-gap for T sited H.

GaAs is more complicated than Si or diamond because of the presence of two different elements. For this reason we looked at stoichiometric clusters saturated with H. We mainly used a 56 atom cluster $Ga_{13}As_{13}H_{30}$ to investigate defects in GaAs. Relaxing the inner 8 atoms gave an average Ga – As bond length of 2.4Å or an error of 2%. A Mulliken bond population revealed a charge build up in the bonds principally coming from Ga atoms. The band gap is 3.5 eV. The size of this gap is typical of clusters terminated with relaxed H atoms. Distorting the structure allowed us to calculate bond stretching and bending force constants between the nearest neighbours. These gave an optic mode frequency at Γ of 8.9 THz. The observed values are 8.8 and 8.1 THz and are split because of the long range Coulomb forces. A single neutron H atom inserted into this cluster preferred to sit at the tetrahedral interstitial site. However the energy difference with the bond centred site is so low (0.2 eV) that we feel that this result may be reversed with a larger cluster. In the bond centred site the partially occupied level occurs close to Ec and in the lower half of the gap for the tetrahedral sited interstitial. This suggests that H in n-GaAs would lie at or close to a T-site and at a BC site in p-GaAs. This is substantially what we have found. A Be atom inserted at a Ga site behaves as an acceptor with a partially filled level around the valence band top (Ev). A H atom inserted into the BC site, between the Be and an adjacent As atom, filled this level hence neutralising the acceptor. The stretch frequency of the H was found to be 2083 cm^{-1} which compares well with the observed one at 2037 cn^{-1} [42].

Si when substituting a Ga site remains on-site with a Si – As bond length of 2.38Å. It has a donor level close to Ec. H inserted into an anti-bonding site along [$-1-1-1$] caused the Si – As bond along [III] to break. The Si moved towards a planar configuration with the three surrounding bonded As atoms. The highest filled level is pushed within 0.3 eV of E_v effectively neutralising the donor. The H stretch and bend frequencies were 1773 cm^{-1} and 1002, 991 cm^{-1} respectively (for an 86 atom cluster; a 56 atom one is inadequate as the H atom lies near the surface). This compares with observed values of 1717 and 896 cm^{-1} [42]. The structures of the H complexes were first determined from infra-red absorption experiments but it is gratifying that these as initio calculations predicted the breaking of the Si – As bond for the hydrogenated sample and this explains the absence of a local vibrational mode associated with the motion of the Si atom parallel to the C_{32} axis. According to recent calculations by us [44] the local modes of Si in the hydrogenated material occur at 416 and 189 cm^{-1}. The former is two-fold degenerate (observed to lie at 410 cm^{-1} [42]) and the latter is the stretch mode which is unobservable because it falls within the one-phonon band. This illustrates a great strength of ab-initio calculations in determining the structure and properties of complicated defects and complements the powerful techniques of Raman and infra-red absorption experiments.

Acknowledgements

I thank many colleagues and friends for collaboration and helpful discussions over parts of this work. In particular I thank Patrick Briddon, Malcolm Heggie, Grenville Lister, Ron Newman, Marshall Stoneham and Andrei Umerski.

References

[1] Lundquist S. March NH"Theory of the Ingomogenous Electron Gas". Plenum Press, London, 1986
[2] Bachelet GB. Hamann DR. Schluter M. "Pseudopotentials that work: from H to Pu", *Phys. Rev.*, **B26**. 4199–228 (1982)
[3] Ihm J. "Total energy calculations in solid state physics". *Rept. Progress in Physics*, **51**, 105–142 (1988)
[4] Ihm J. Zunger A. Cohen ML. "Momentum space formalism for the total energy of solids", *J. Phys. C (Solid St. Phys.)*, **12**, 4409–422 (1979)
[5] Yin MT. Cohen ML. "Theory of ab-initio pseudopotenial calculations". *Phys. Rev.*, **25**, 7403–7412 (1982)
[6] Car R, Parrinello M."Unified approach for molecular dynamics and density functional theory", *Phys. Rev. Lett*, **55**. 2471 (1984)
[7] Payne MC. Needels M. Joannopoulos JD. "Ab initio calculations of the structure of a grain boundary by simulated annealing".*Phys. Rev. Lett*, **58**. 1348 (1987)
[8] Gillan MJ. "Calculation of the vacancy formation energy in aluminium". *J Phys F*, to be published (1989)
[9] Van de Walle CG, Bar-Yam Y. Pantiledes ST. "Theory of H diffusion and reactions in crystalline Si", *Phys. Rev. Lett.*, **60**. 2761 (1988)
[10] Chang KJ. Chadi DJ. "Passivation of shallow level dopants in crystalline Si", *Phys. Rev.*, **60**, 1422–25 (1988)

[11] Anderson OK, "Linear methods in band theory", *Phys. Rev.,* **B12**, 3060 (1975)

[12] Moruzzi VL, Janak JL, Williams AR, "Calculated Properties of Metals", Pergammon Press, New York (1978)

[13] Chelikowsky JR, Louie SG, "First principles LCAO method for cohesive and structural properties of solids: "application to diamond", *Phys. Rev.*, **B29** 3740 (1984)

[14] Mednick K, Lin CC, "Self-consistent electronic structure of Cl adsorbed onto the Se (111) surface", *Phys. Rev.*, **17** 4807-20 (1978)

[15] Baraff GA, Schluter M, "Green function methods in total energy calculations", *Phys. Rev.*, **B19**, 4656 (1979)

[16] Slater JC, Johnson KH, "Self consistent field cluster methods for polyatomic molecules and solids", *Phys. Rev. B5*, **844** (1972)

[17] Redondo A, Goddard WA III, McGill TC, Surratt GT, "Relaxation of (III) Si surface atoms from studies of Si_4H_9", *Solid State Common.*, **20**, 733-6 (1976)

[18] Bernhole J, Holzwarth NAW, "Local density pseudopotential calculations for molecules", *J Chem Phys*, **81**, 3987-95 (1984)

[19] Averill FW, Ellis DE,"An efficient numerical multicentre basis set for MO calculations: application to $FeCl_4$", *J Chem Phys*,**59**, 6412 (1973)

[20] Baerends, Ellis DE, Ros P, "Self-consistent HFS calculations: computational procedure", *Chem Phys*, **2**, 41 (1973)

[21] Harris J, Muller JE, "Local Density Approximations in Quantum Chemistry and Solid State Physics", ed JP Dahl and J Avery, Plenum Press, New York (1984)

[22] Jones R, Sayyash A, "Approximations in local density functional calculations for moleculs and clusters: application to C_2 and H_2O", *J. Phys. C*, **19**, L653-7,(1986)

[23] Inglesfield JE, "A method of embedding", *J. Phys. C*, **14**, 3795 (1981)

[24] Baraff GA, Schluter M, "The LCAO approach to the embedding problem", *J. Phys. C (Solid St. Phys.)*, **19**, 4383-91 (1986)

[25] Fisher AJ, "Methods of embedding for defects and surface problems", *J. Phys. C (Solid St. Phys.)*, **21**, 3229-49 (1988)

[26] Jones R., "The Phonon spectrum in diamond derived from ab-initio local density functional calculations on atomic clusters", *J Phys. C:Solid state Phys.*, **21**, 5735 (1988)

[27] Dunlap BI, Connolly IWD, Sabin JR, "On some approximations in application of X-alpha theory", *J Chem Phys*, **71**, 3396-402 (1979).

[28] Jones R., "Ab-initio calculations of the phonon spectrum in Si using small atomic clusters", *J Phys. C*, **20**, L271-3 (1987)

[29] Jones R., "Local density functional calculations of the structure and vibratory modes of the substitutional C impurity in Si", *J Phys. C*, **20**, L713-6 (1987)

[30] Keating PN, "Effect of invariance requirements on elastic strain energy of crystals with application to the diamond structure", *Phys. Rev.*, **145**, 637-45 (1966)

[31] Baraff CA, Kane EO, Schluter M,"Enfeebled oxygen bonding and metastability in GaP:O", *Phys. Rev.*, **B25**, 548-60 (1982)

[32] Zur A, McGill TC, Goddard WA III, "Generalised valence bond theory and force constants in Si", Proc. 13th Int. Conf. on Defects in Semiconductors, Coronado, Warringdale, PA:Metallurgic Soc. of AIME (1984)

[33] Kune K,"Ab initio calculations of phonon spectra in solics", Proc of Nato Advanced Summer Study Inst. "Electronic Structure: Dynamics and Quantum Structural Properties of Condensed matter", Series B vol 121, ed JT Devreese, P Van Camp, New York, Plenum (1985)

[34] Musgrave MJP, Pople JA, "A general valence force field for diamond", *Proc Roy Soc* **A268**, 474-84 (1962)

[35] Newman RC, Smith RS, "Vibrational absorption of carbon and carbon-oxygen complexes in Si", *J. Phys. Chem. Solids*, **30**, 1493 (1969)

[36] Briddon P, Jones R, Lister GMS, "Hydrogen in diamond", *J. Phys. C (Solid St. Phys.)*, **21**, L1027-31 (1988)

[37] Briddon P, Jones R, "Ab-initio calculations of the passivation of shallow impurities in GaAs", Proc of Linkoping Conf. on Defects in Semiconductors, to be published, (1988)

[38] Holzschuh E, Kundig W, Meier PF, Patterson BD, Sellschop JPF, Stemmet MC, Appel H, "Muonium in diamond", *Phys. Rev.* **A25**, 1272-86 (1982)

[39] Claxton TA, Evans A, Symonds MCR, "Self-consistent field cluster investigation of muonium related paramagnetic centres in diamond", *J Chem. Soc. Faraday. Trans. II*, **82**, 2031-4 (1986)

[40] Estle TL, Estreicher S, Marynick DS,"Bond centred H or muonium in diamond: the explanation for anamolous muonium and an example of metastability", *Phys. Rev. Lett.*, **58**, 1547-50 (1987)

[41] Mainwood A, Stoneham AM, "Interstitial muonium and hydrogen in diamond and silicon", *J. Phys. C (Solid SAt. Phys.)*, **17**, 2513-24 (1984)

[42] Nandhra PS, Newman RC, Murray R, Pajot B, Chevallier J, Beall RB, Harris JJ, "Passivation of Be acceptors in GaAs by exposure to a hydrogen plasma", *Semicon. Sci. and Tech.*, **3**, 356-60 (1988)

[43] Pajot B, Newman RC, Murray R, Jajil A, Chevallier J, Azoulzy R, "High resolution infrared study of the neutralisation of silicon donors in GaAs", *Phys. Rev.*, **37**, 4188-95 (1988)

[44] Briddon P, Jones R, unpublished.