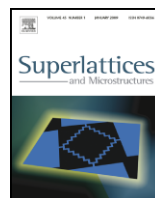




ELSEVIER

Contents lists available at ScienceDirect

## Superlattices and Microstructures

journal homepage: [www.elsevier.com/locate/superlattices](http://www.elsevier.com/locate/superlattices)

# Empirical pseudopotential band structure parameters of 4H-SiC using a genetic algorithm fitting routine

G. Ng\*, D. Vasileska, D.K. Schroder

School of Electrical, Computer and Energy Engineering, Arizona State University, Tempe, AZ 85287-5706, USA

## ARTICLE INFO

### Article history:

Received 29 September 2010

Received in revised form

2 November 2010

Accepted 17 November 2010

Available online 25 November 2010

### Keywords:

Silicon carbide

Empirical pseudopotential method

Genetic algorithm

## ABSTRACT

In this paper, the viability of using a genetic algorithm to find band structure parameters for empirical pseudopotential method (EPM) calculations is demonstrated by applying a genetic algorithm to find the EPM parameters for 4H-SiC. The form of the pseudopotential for 4H-SiC and the 19 form factors found by the genetic algorithm to fit the band structure to experimentally measured indirect energy gap and direct optical gaps are given. In addition, the effective masses for the conduction band minimum are extracted from the calculated band structure. It is shown that the genetic algorithm provides an effective, automated way to find parameters that give reasonably good fits to both the band gaps and the effective masses simultaneously.

© 2010 Elsevier Ltd. All rights reserved.

## 1. Introduction

Over the past few decades, interest in silicon carbide (SiC) has been increasing because of its potential applications in high-temperature, high-power and high-frequency electronics. The usefulness of SiC in these applications stems largely from its wide band gap energy of the various SiC polytypes. The 4H polytype in particular has drawn attention because its band gap energy is the largest of all the SiC polytypes that can be grown in bulk form [1]. Considering the extreme environments and operating conditions the material is foreseen to be used in, a solid understanding of the electronic band structure as well as ways to calculate it will be instrumental to the further development of 4H-SiC devices.

One way to calculate the band structure is through the empirical pseudopotential method (EPM). The EPM provides an effective way of obtaining the band structure since it is adjustable to fit measured optical band gaps. The problem that arises is finding the correct parameters that lead to a satisfying

\* Corresponding author. Tel.: +1 510 579 6961.

E-mail address: [garrick.ng@asu.edu](mailto:garrick.ng@asu.edu) (G. Ng).

fit of the experimental results. This is especially challenging for materials with a large unit cell, such as SiC, since many more parameters are needed for the calculation. The most common approach to this problem is a semi-empirical one that uses the atomic pseudopotentials of Si and C, perhaps with some modification, in the hope that they are transferable to the SiC system. The first study to use such an approach was carried out by Junginger and van Haeringen in 1970 [2]. More recently, Pennington and Goldsman used pseudopotentials of Si and C modified to account for nonlocal screening effects to obtain the EPM form factors [3]. Zubkova et al. also used the semi-empirical EPM, based on the same pseudopotentials used by Junginger et al., to study the temperature dependence of the band structure [4]. Another alternative is to fully exploit the flexibility offered by the EPM by abandoning attempts to obtain the form factors from atomic potentials and instead treat them as completely adjustable parameters. This is the approach used in this paper, and the form factors are found in an automated way through the use of a genetic algorithm developed in this study.

Genetic algorithms have been utilized in a variety of disciplines to optimize parameters of multi-dimensional functions. Within the area of band structure calculations, genetic algorithms were first demonstrated by Starrost et al. as being effective in adjusting up to eleven tight-binding parameters to fit the energy band gaps of various zincblende semiconductors [5]. Klimeck et al. have also used genetic algorithms to adjust up to 20 parameters in a second-nearest neighbor tight-binding model to fit effective masses as well as band gap energies [6]. In addition, genetic algorithms have been employed in inverse band structure calculations to find atomic configurations and lattice constants in order to engineer materials with a given band structure [7,8]. Genetic algorithms have thus been shown to be effective in providing an automated way to search for and to optimize tight-binding calculations with an arbitrary number of parameters. Here it will be shown that this strategy can be equally effective in finding band structure parameters for an EPM calculation.

## 2. The empirical pseudopotential method

The starting point for the EPM is the one electron Schrödinger equation given by

$$\left[ \frac{-\hbar^2}{2m_0} \nabla^2 + V_{PS}(\mathbf{r}) \right] \psi_{\mathbf{k}} = E_{\mathbf{k}} \psi_{\mathbf{k}} \quad (1)$$

where  $\hbar$  is the reduced Planck's constant,  $m_0$  is the electron free mass,  $V_{PS}(\mathbf{r})$  is the crystal pseudopotential,  $\psi_{\mathbf{k}}$  is the pseudo wave function of the valence electrons, and  $E_{\mathbf{k}}$  are the energy eigenvalues that make up the band structure. The valence electrons are assumed to be weakly bound to their host atoms so that  $\psi_{\mathbf{k}}$  can be expanded into a Fourier series of plane waves,

$$\psi_{\mathbf{k}} = \frac{\exp(i\mathbf{k} \cdot \mathbf{r})}{\sqrt{\Omega}} \sum_{\mathbf{G}} C_{\mathbf{k}+\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{r}) \quad (2)$$

where  $\Omega$  is the volume of the unit cell,  $C_{\mathbf{k}}$  are the expansion coefficients and  $\mathbf{G}$  are the reciprocal lattice vectors of the Bravais lattice. Using the wave function of Eq. (2) in Eq. (1) and taking the inner product with any plane wave component results in the secular equation

$$\det \left[ \left[ \frac{\hbar^2}{2m_0} |\mathbf{k} + \mathbf{G}|^2 - E_{\mathbf{k}} \right] \delta_{\mathbf{G},\mathbf{G}'} + V_{\mathbf{G},\mathbf{G}'} \right] = 0. \quad (3)$$

The off-diagonal matrix elements of the pseudopotential  $V_{\mathbf{G},\mathbf{G}'}$  are given by

$$V_{\mathbf{G},\mathbf{G}'} = \frac{1}{\Omega} \int V_{PS}(\mathbf{r}) \exp[i(\mathbf{G}' - \mathbf{G}) \cdot \mathbf{r}] d\mathbf{r} \quad (4)$$

which is just the Fourier transform of the pseudopotential from real space to reciprocal space, and are known as pseudopotential form factors.

The form that  $V_{\mathbf{G},\mathbf{G}'}$  takes can be deduced by examining the locations of the atoms within the unit cell of the system under consideration. For 4H-SiC, with a hexagonal crystal structure, the unit

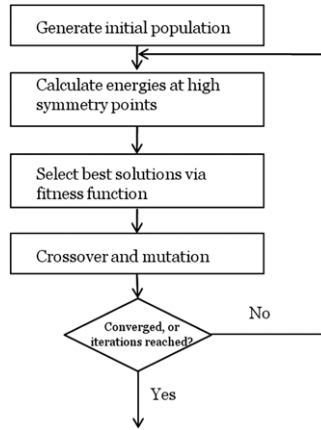


Fig. 1. Flowchart of the genetic algorithm for band structure calculations.

cell is formed of four pairs of Si–C dimers stacked in an ABCB sequence. This leads to the crystal pseudopotential expression

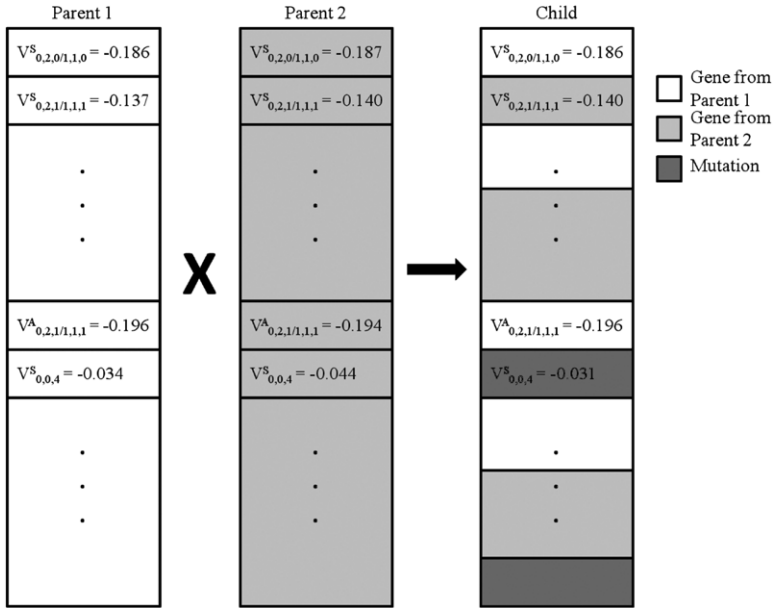
$$V_{\mathbf{G},\mathbf{G}'} = [V_{\mathbf{G}}^S \cos((\mathbf{G}' - \mathbf{G}) \cdot \mathbf{s}) + iV_{\mathbf{G}}^A \sin((\mathbf{G}' - \mathbf{G}) \cdot \mathbf{s})] \times \left[ 1 + e^{-i(\mathbf{G}' - \mathbf{G}) \cdot (\mathbf{v} + \mathbf{h}_B)} + e^{-i(\mathbf{G}' - \mathbf{G}) \cdot (2\mathbf{v} + \mathbf{h}_C)} + e^{-i(\mathbf{G}' - \mathbf{G}) \cdot (3\mathbf{v} + \mathbf{h}_B)} \right] \quad (5)$$

where  $V_{\mathbf{G}}^S$  and  $V_{\mathbf{G}}^A$  are the symmetric and anti-symmetric Fourier components of the pseudopotential to be used for fitting. The remaining vectors in Eq. (5) are defined as  $\mathbf{s} = L_z/2 \hat{\mathbf{z}}$ ,  $\mathbf{v} = c/4 \hat{\mathbf{z}}$ ,  $\mathbf{h}_B = a/2 \hat{\mathbf{x}} + a/2\sqrt{3} \hat{\mathbf{y}}$ , and  $\mathbf{h}_C = a/\sqrt{3} \hat{\mathbf{y}}$ , where  $L_z$  is the bond length between the Si and C pairs, and  $c$  and  $a$  are the hexagonal lattice constants for 4H-SiC.

### 3. Procedure for the genetic algorithm fitting

Using Eq. (5) for the crystal pseudopotential, the genetic algorithm was implemented to find optimal values for the form factors to fit the calculated band structure to experimental data. The strategy of a genetic algorithm is very similar to evolutionary processes in the real world. The optimization proceeds by first randomly generating a population of possible solutions. The set of parameters of the problem is identified as the “chromosome” that makes up a solution. Each of the possible solutions are evaluated according to a pre-defined weighting scheme. The most “fit” of the solutions are chosen to survive and kept within the population, while the underperforming solutions are discarded. The population is then replenished by having the fittest solutions “reproduce”—they create new solutions in a process called “crossover” by randomly taking parameters from two existing fit solutions. In order to create solutions with parameters having values not previously existing in the original population, genes may randomly “mutate” to take on new values. The cycle is repeated until the solutions converge or a preset number of iterations have been carried out. Thus, the genetic algorithm has four steps: initialization of the original population, selection of solutions based upon a fitness evaluation, reproduction through crossover and mutation to create new solutions, and termination of the process after some criterion is met. A flow chart of this process is shown in Fig. 1. The algorithm is largely stochastic; nevertheless, genetic algorithms have been frequently observed to successfully produce reasonable solutions.

A critical aspect of any genetic algorithm is the implementation of the “gene encoding”, which refers to how the variables of interest are parameterized. Typically, one of the two different approaches are employed. One method is to convert all the parameters into binary strings which are then concatenated into one long string, often referred to as a “chromosome”. Portions of these strings are then randomly chosen between parent solutions in the reproduction step of the algorithm



**Fig. 2.** Illustration of the real-valued parameter encoding, and the crossover and mutation operations in the reproduction step. Each of the parameters is interpreted as a “gene”, with each gene of the child either inherited from a random parent or being a new value generated by mutation.

to create the child solutions. The other approach is to treat each of the parameters as genes, keeping their real values for the encoding. The set of genes is then considered as the chromosome, with each gene of the child either randomly inherited from one of the two parents or taking on a new value through mutation during the reproduction step. In this study, a large number of EPM form factors lends itself to the latter of these approaches. The form factors  $V_G^S$  and  $V_G^A$  are identified as the genes, and in the reproduction step these form factors are generated by the aforementioned crossover or mutation operations. An illustration of this process is shown in Fig. 2.

The evaluation of how well each solution performs is done through the use of an objective function. The objective function is similar to the ones used in previous studies [5,6] and is given by

$$d(\mathbf{m}) = - \left( \frac{1}{\sum_n w_n} \left[ \sum_{n'} w_{n'} (E_{n'}(\mathbf{m}) - E_{n',tar})^2 \right] \right)^{1/2} \tag{6}$$

where  $d(\mathbf{m})$  is the fitness of a solution calculated with the set of parameters  $\mathbf{m}$ ,  $E_n(\mathbf{m})$  are the energies calculated with the set of parameters  $\mathbf{m}$ ,  $E_{n,tar}$  are the targeted goal values for energy  $n$ , and  $w_n$  is a weight chosen from an interval [1,100] based on the importance of that energy. The difference between the calculated energy and the targeted value is squared to penalize larger deviations from the goal values. The negative sign in front of Eq. (6) drives the algorithm to maximize  $d(\mathbf{m})$ ; however, the algorithm can just as well become a minimization problem by removing the negative sign. Hard minimum or maximum values for particularly important energies can also be included by setting Eq. (6) to an arbitrarily low value if the calculated energy falls out of an acceptable range.

#### 4. Results

For this study, the targeted energies include as many of the published experimental data on the electronic structure of 4H-SiC as possible. This includes the indirect  $\Gamma$  to  $M$  band gap energy, the direct energy transitions at the  $\Gamma$ ,  $M$ ,  $K$  and  $L$  points, and the total valence band energy. The indirect,

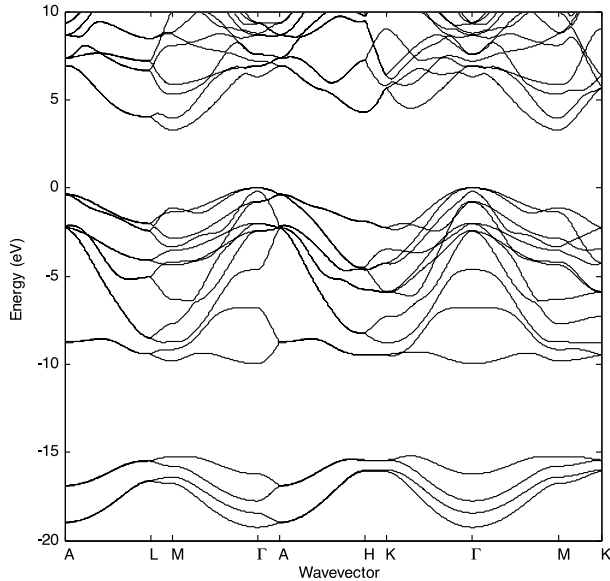


Fig. 3. Band structure of 4H-SiC fitted using the genetic algorithm routine.

$\Gamma$  to  $M$  band gap energy of 4H-SiC was first measured by Choyke et al., for which a value of 3.263 eV was obtained [9]. This is still the most widely quoted experimental value for the band gap energy to this day. Optical measurements by Ahuja et al. gave the direct gap energies at the  $\Gamma$ ,  $M$ ,  $K$  and  $L$  high symmetry points as 6.2 eV, 4 eV, 7.8 eV and 6.7 eV, respectively, and a total valence band energy of 18.2 eV [10]. Electroreflectance measurements by Demir et al. supported those values, giving the direct gap energy at the  $\Gamma$  and  $M$  points as 6.18 eV and 4.5 eV, respectively [11].

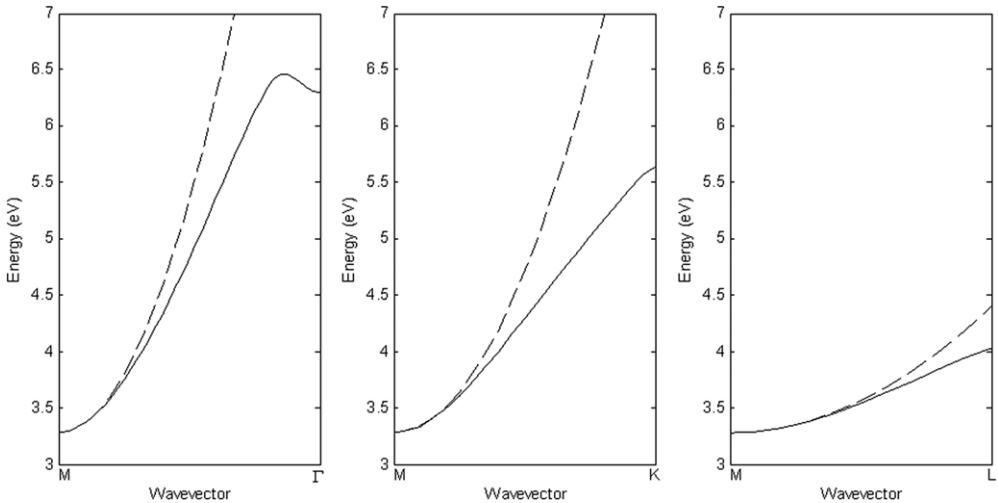
For the calculation, a total of 575 plane waves for a cutoff energy of 205 eV were chosen since this lies in a range that has been observed to give good convergence results in diamond and zincblende materials [12]. The lattice constants of  $a = 3.032 \text{ \AA}$  and  $c = 9.928 \text{ \AA}$ , and bond length of  $L_z = 1.866 \text{ \AA}$  were used [13]. The genetic algorithm sought solutions by varying 19 form factors in a range between  $-0.25 \text{ Ry}$  and  $0.25 \text{ Ry}$ , discretized into units of  $0.001 \text{ Ry}$  (see Fig. 1). An initial population of 200 solutions was used, with half the population replaced after each iteration. A variable mutation probability was employed, varying linearly from about 6% for two solutions with no complementary form factors in common to about 17% for two duplicate solutions. In total, the genetic algorithm was run for about 250 iterations before being terminated. The resultant band structure is plotted along several high symmetry points of the hexagonal structure in Fig. 3, while the form factors are given in Table 1. The fit arrived at by the genetic algorithm is very satisfactory compared to the experimental values. The band gap energy arrived at is 3.28 eV, while the direct  $\Gamma$ ,  $M$ ,  $K$  and  $L$  energy transitions obtained are 6.30 eV, 4.42 eV, 7.90 eV and 6.03 eV, respectively. The total valence band is 19.25 eV wide. Comparatively, the EPM calculation by Zubkova et al. give a band gap energy smaller by about 0.3 eV, a direct  $\Gamma$  transition smaller by 1.6 eV and a direct  $L$  transition smaller by more than 1.5 eV. The EPM calculation by Pennington et al. underestimates the direct  $\Gamma$  transition by more than 1 eV and overestimates the direct  $M$  transition by about the same energy. At the same time, the calculation has been simplified by requiring 12 less fitting parameters.

Using this band structure, the electron effective masses along the  $M$ - $\Gamma$ ,  $M$ - $L$  and  $M$ - $K$  directions were calculated. As shown in Fig. 4, this was done by fitting a parabola to the lowest 0.05 eV portion of the conduction band minimum, where the majority of electrons reside at room temperature, using a least squares fit. The values of the effective masses obtained are  $m_{M\Gamma}^* = 0.66m_0$ ,  $m_{MK}^* = 0.31m_0$  and  $m_{ML}^* = 0.34m_0$ , which are in good agreement with the experimentally measured values of  $m_{M\Gamma}^* = 0.58m_0$ ,  $m_{MK}^* = 0.29m_0$  and  $m_{ML}^* = 0.33m_0$  [14]. Table 2 shows a comparison between the values

**Table 1**

EPM form factors for 4H-SiC determined by the GA, grouped together by reciprocal lattice vectors with the same magnitude, where  $k_x$  is scaled by  $a/2\pi$ ,  $k_y$  is scaled by  $a\sqrt{3}/2\pi$ , and  $k_z$  is scaled by  $c/2\pi$ . Not included are form factors for which the reciprocal lattice vectors cause the structure factor to vanish. Values of the form factors are in Rydbergs.

$\mathbf{G}$	$V^S$	$V^A$
(0, 2, 0) (1, 1, 0)	-0.186	
(0, 2, 1) (1, 1, 1)	-0.140	-0.196
(0, 0, 4)	0.103	-0.031
(0, 2, 2) (1, 1, 2)	-0.111	-0.034
(0, 2, 3) (1, 1, 3)	-0.022	-0.007
(0, 2, 4) (1, 1, 4)	-0.107	-0.094
(0, 2, 5) (1, 1, 5)	-0.034	-0.058
(2, 0, 0) (1, 3, 0)	0.085	
(0, 2, 6) (1, 1, 6)	0.041	-0.124
(0, 4, 0) (2, 2, 0)	0.004	
(0, 4, 1) (2, 2, 1)	0.007	0.003



**Fig. 4.** Shape of the calculated (-) lowest conduction band along the  $M-\Gamma$ ,  $M-K$  and  $M-L$  directions, fitted with a least square parabolic approximation (- -).

of the energy transitions and effective masses obtained from this study and previous experimental measurements.

**Table 2**

Energy transitions of the indirect and the direct band gap at high symmetry points  $\Gamma$ ,  $M$ ,  $K$  and  $L$ , and effective masses of 4H-SiC calculated in this work compared to experimental results. The energy transitions are in eV, while the effective masses are in units of  $m_0$ .

	Energy transitions					Effective masses		
	$E_g$	$\Gamma$	$M$	$K$	$L$	$m_{M\Gamma}$	$m_{MK}$	$m_{ML}$
Expt.	3.26 <sup>a</sup>	6.18 <sup>b</sup> , 6.2 <sup>c</sup>	4 <sup>c</sup> , 4.5 <sup>b</sup>	7.8 <sup>c</sup>	6.7 <sup>c</sup>	0.58 <sup>d</sup>	0.29 <sup>d</sup>	0.33 <sup>d</sup>
This work	3.28	6.30	4.42	7.9	6.03	0.66	0.31	0.34

<sup>a</sup> Ref. [8].

<sup>b</sup> Ref. [10].

<sup>c</sup> Ref. [9].

<sup>d</sup> Ref. [13].

## 5. Conclusion

In conclusion, a set of parameters and an expression for the crystal pseudopotential required for an EPM calculation of the band structure of 4H-SiC is provided. These form factors were determined using a genetic algorithm as an automated fitting routine. A good fit to the experimentally measured energy transitions and effective masses was found. At the same time, the calculation was simplified compared to previous calculations by using fewer fitting parameters. Therefore, the viability of using genetic algorithms as a fast and efficient method in fitting EPM band structure calculations has been demonstrated.

## References

- [1] A.A. Lebedev, *Semicond. Sci. Technol.* 21 (2006) R17.
- [2] H.G. Junginger, W. van Haeringen, *Phys. Status Solidi* 37 (1970) 709.
- [3] G. Pennington, N. Goldsman, *Phys. Rev. B* 64 (2001) 045104.
- [4] S.M. Zubkova, L.N. Rusina, E.V. Smelyanskaya, *Semiconductors* 37 (2003) 257.
- [5] F. Starrost, S. Bornholdt, C. Solterbeck, W. Schattke, *Phys. Rev. B* 53 (1996) 12549.
- [6] G. Klimeck, R.C. Bowen, T.B. Boykin, C. Salazar-Lazaro, T.A. Cwik, A. Stoica, *Superlattices Microstruct.* 27 (2000) 77.
- [7] P. Piquini, P.A. Graf, A. Zunger, *Phys. Rev. Lett.* 100 (2008) 186403.
- [8] Y.H. Zheng, *Superlattices Microstruct.* 48 (2010) 343.
- [9] W.J. Choyke, D.R. Hamilton, L. Patrick, *Phys. Rev.* 133 (1964) A1163.
- [10] R. Ahuja, A. Ferreira da Silva, C. Persson, J.M. Osorio-Guillen, I. Pepe, K. Jarrendahl, O.P.A. Lindquist, N.V. Edwards, Q. Wahab, B. Johansson, *J. Appl. Phys.* 91 (2002) 2099.
- [11] G. Demir, T.E. Renfro, R. Glosser, S.E. Saddow, *Appl. Phys. Lett.* 84 (2004) 3540.
- [12] M.L. Cohen, T.K. Bergstresser, *Phys. Rev.* 141 (1966) 789.
- [13] P. Käckell, B. Wenzel, F. Bechstedt, *Phys. Rev. B* 50 (1994) 17037.
- [14] W.R.L. Lambrecht, B. Segall, *Phys. Rev. B* 52 (1995) R2249.