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Radiation Damage of Diamond by Electron and Gamma Irradiation

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Diamond is an exceptionally radiation-hard material, but the main mechanisms by which lattice damage results from irradiation of high-energy particles and photons are not well understood. Models of radiation damage in diamond have been built up for both electron and gamma irradiation using Monte Carlo computer simulations. The energies investigated ranged from 0.25 to 10 MeV for electron irradiation and 1 to 15 MeV for gamma irradiation. Electrons have a low collision cross-section with carbon atoms, and therefore much of their energy is dissipated in ionisation before the electron displaces an atom. Gamma radiation causes damage by the indirect process of generating electrons (by Compton scattering and pair production) which then displace atoms (and ionise the material). The knock-on atom may cause further damage by displacing further atoms. However, both electron and gamma irradiation form predominantly isolated vacancies and interstitial pairs (Frenkel pairs). The range of 1 MeV electrons in diamond is about 1.3 mm with a nearly constant damage profile up to this cut-off. The range of gamma photons is much greater, with about 85% of 1 MeV photons passing through a 5 mm diamond without causing any damage. The total damage rates were calculated to vary between 0.01 and 5.15 vacancies per incident electron and between 0.02 and 6.10 vacancies per photon over the energy ranges investigated.

1. Introduction

Diamond has a reputation for being radiation-hard. Therefore it is being suggested as a suitable semiconductor for detectors in high-radiation environments such as the Large Hadron Collider at CERN [1]. Its response to radiation damage has been investigated by a series of experiments [2 to 8], which, as expected, show that diamond detectors could survive very much longer than silicon devices in high-radiation environments. However, these experiments have usually been concerned with the effect of the radiation damage on the electronic properties of the diamond, but have not investigated the defects caused by the radiation or their distribution in the crystal. Some early work on radiation damage of diamond, on the other hand, looked at the production of vacancies and other defects detected by optical and electron paramagnetic spectroscopy (EPR) [9] and studies of radiation damage by these techniques have continued. The vacancy in diamond is one of the best understood defects in any material [10], and the self-interstitial has recently been identified [11] – one of the few self-interstitials in any semiconductor to be detected experimentally [12]. The production of more complex defects, for example, the di-vacancy, the di-interstitial and nitrogen–vacancy complexes under various radiation conditions, is underway at the moment.

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In experimental studies, electron irradiation is often used to produce damage. Even with electrons of energy 1 to 2 MeV, the quoted rates for vacancies produced vary widely in the literature, partly because the temperatures of irradiation are not always well-controlled [13]. There is a difference with crystallographic direction, but this is insignificant compared to the reported discrepancies. There has been very little attempt to compare the damage rates or production as a function of depth for different particles (neutrons, protons, alpha [14] or more exotic particles or gamma rays).

In Sections 2 and 3 of this paper we will discuss how particles and electromagnetic radiation, respectively, can damage the diamond crystal. This allows us to set up computer models to predict the rates and depth profiles of the damage in Section 4, and to show their results in Section 5. We will then discuss briefly, in Section 6, the annealing of that damage, which may take place as the irradiation proceeds reducing the damage that is detected.

2. The Mechanisms of Radiation Damage by Electrons

2.1 Rutherford scattering

The radiation damage of diamond that persists after the radiation ceases includes the displaced atoms (interstitials) and vacancies, which are produced when the reaction on the atom when it scatters the particle is strong enough to displace the atom from its lattice position. For an incident charged particle of mass m, charge Z and energy E, a host atom (of mass M) will be displaced if after the collision it has an energy greater than a value known as the displacement energy E_d. The values of E_d quoted in the literature range from 25 [15], 35 [13] to 80 eV [9], with most of the recent literature agreeing on the 30 to 40 eV range. The conservation of momentum (relativistic) gives us values for the maximum energy E_{max} with which atoms can be displaced [15],

$$E_{max} = \frac{2ME(E + 2mc^2)}{(m + M)^2 c^2 + 2ME} . \tag{1}$$

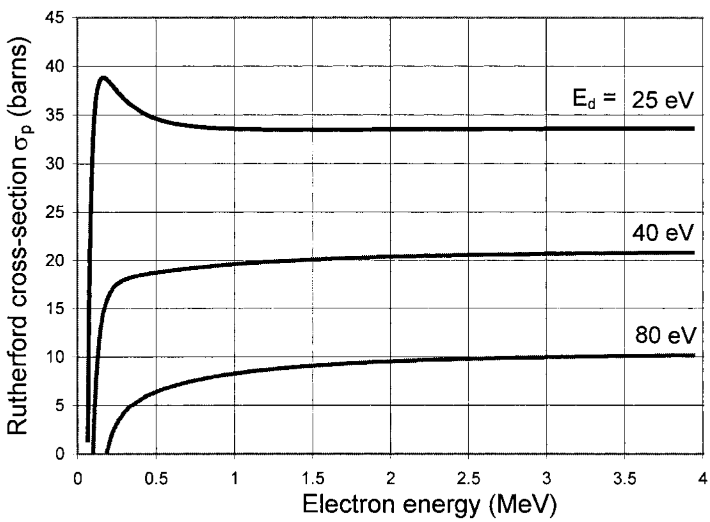

Fig. 1. Variation of Rutherford cross-section with electron energy, for three values of the displacement energy E_d (25, 40 and 80 eV). 40 eV was the value used in the simulations

This means that electrons of lower energy than 145 to 186 keV (for E_d = 30 to 40 eV) cannot cause radiation damage in diamond. Values of E_d near 40 eV are supported by low-energy electron irradiation experiments, which give a range of 180 to 220 keV, depending on crystallographic direction [16]. For this reason, the value of E_d used in the rest of this analysis is 40 eV.

The cross-section for this process for a relativistic particle [17] is

$$\sigma = \frac{4Z^2 E E_{\max}}{mc^2 E_d}\left(\frac{1-\beta^2}{\beta^4}\right) \times\left[1+2\alpha\beta\pi\sqrt{\frac{E_d}{E_{\max}}}-\frac{E_d}{E_{\max}}\left\{1+2\alpha\beta\pi+\left(\beta^2+\pi\alpha\beta\right)\ln\left(\frac{E_{\max}}{E_d}\right)\right\}\right], \quad (2)$$

where α is the fine structure constant $=1/137$, and β is the ratio of the velocity of the electron, v, to the speed of light, c. Figure 1 shows the cross-section as a function of energy for three values of the displacement energy (25, 40 and 80 eV).

2.2 Knock-on atoms

If a particle displaces an atom from its lattice site and the displaced atom has sufficient energy, it may displace further atoms. This is particularly significant where the particle is heavy (a neutron, proton or alpha) and transfers a large momentum to the knock-on atom, where a large damage cascade may result from the original collision. These damage cascades may not be detected as single vacancies, although they may affect the electronic properties of the diamond by trapping electrons or holes, leading to confusing assessments of the damage caused by the particles. Of course, the cross-section for a carbon–carbon collision is much greater than for a particle–carbon collision, so the damage cascade occurs within a small distance compared to the length of the particle track. Fortunately, the problem of how the knock-on atoms damage the diamond is familiar to those who implant carbon ions into diamond. There have been many ion-implantation studies of diamond [18]. A very well-tested computer program (TRIM [19]) can predict accurately the distribution of the knock-on atoms and the trail of damage that they leave.

2.3 Energy lost to ionisation

As a charged particle passes through a material, provided its velocity is greater than that of the electrons in the solid, it will ionise the material – that is, it will leave a trail of electron–hole pairs in a semiconductor. The energy loss as a function of penetration distance z, can be derived from the Bethe-Bloch equation [20]

$$\left(\frac{\partial E}{\partial z}\right)_i = \frac{4\pi E^4 NZ}{mv^2} \times\left[\ln\left(\frac{2mc^2}{I}\right)+\ln(\gamma-1)+\frac{1}{2}\ln(\gamma+1) -\frac{1}{2}\left(3+\frac{2}{\gamma}-\frac{1}{\gamma^2}\right)\ln 2+\frac{1}{16}-\frac{1}{8\gamma}+\frac{9}{16\gamma^2}\right], \quad (3)$$

where I is the ionisation energy of the diamond and N is the electron density. γ is the relativistic quantity $\gamma = (1 - \beta^2)^{-1/2}$.

This is true of the incident particles or the knock-on atoms, which may have enough energy to be stripped of some of their electrons and move through the crystal as ions. In this case the knock-on atoms (of mass M) are unlikely to be moving at relativistic speeds and equation (3) can be simplified [20] to

$$\left(\frac{\partial E}{\partial z}\right)_i = \frac{4\pi e^4}{Mv^2}\, NZ \ln\left(\frac{\sqrt{2}\, Mv^2}{I}\right). \tag{4}$$

In practice, most of the energy of an incident particle is lost to ionisation and for this reason, charged particles have short ranges in solids.

2.4 Bremsstrahlung radiation

Electrons scattered by lattice atoms will emit bremsstrahlung radiation in the form of X-rays. The energy lost by the electrons is quite small in diamond, because it is a strong function of the atomic number of the atom, Z_C; however, it is significant for high energy electrons. The bremsstrahlung radiation is negligible for heavier particles.

$$\left(\frac{\partial E}{\partial z}\right)_{\text{brems}} = \left[NZ_C(Z_C - 1)\,(E + mc^2)\,\alpha\right]\left(\frac{r_0}{4\pi\varepsilon}\right)^2\left[4\ln\left(\frac{2(E+mc^2)}{mc^2}\right) - \frac{4}{3}\right], \tag{5}$$

where $r_0 = 2.818 \times 10^{-15}$ m is the classical electron radius.

2.5 Other energy losses of particles passing through diamond

In metals, there are significant energy losses due to scattering by conduction electrons. In diamond, this effect is negligible – approximately two orders of magnitude smaller than ionisation losses for 1 MeV electrons.

The energy loss of electrons of energy less than about 100 MeV is given by the sum of equations (3) and (5).

3. Radiation Damage of Diamond due to Gamma Irradiation

We wanted to model the damage due to gamma radiation as well as particles. The nuclear cross-section for direct interaction of gamma rays below about 15 MeV with carbon nuclei is very small. However the gammas interact with the electrons in the solid by three mechanisms: the photoelectric effect, Compton scattering and pair production.

3.1 The photoelectric effect

In this case, the gamma photon is absorbed by a core electron, which is excited into a conduction band state, and de-excites by giving out an X-ray or an Auger electron. In fact, the emitted electrons have too small an energy to damage the crystal, but they do contribute to the attenuation of the gamma rays. The cross-section for gamma rays of energy E_γ is given by [20]

$$\sigma_{\text{PE}} = \frac{32\sqrt{2}}{3}\, r_0^2 \alpha^4 Z_C^5 \eta^{-7/2}, \tag{6}$$

where $\eta = E_\gamma/(mc^2)$.

3.2 Compton scattering

This occurs when the gamma ray is scattered by a valence band electron through an angle θ. The maximum energy of the ejected electron is

$$E_{\max}^{C} = \frac{2\eta E_\gamma}{(1+2\eta)}, \tag{7}$$

which is a high enough energy for this electron to displace lattice atoms by the same mechanisms as we discussed in Section 2. The cross-section for Compton scattering [20] is given by

$$\sigma_C = \pi r_0^2 Z_C \left[\frac{(\eta-3)(\eta+1)}{\eta^3}\ln(1+2\eta) + \frac{2(5\eta^2+9\eta+1)}{\eta^2(1+2\eta)} - \frac{8\eta^2}{3(1+2\eta)^3}\right]. \tag{8}$$

3.3 Pair production

If the gamma energy is greater than twice the mass energy of an electron, then an electron–positron pair may be produced, in the vicinity of a nucleus whose recoil allows momentum to be conserved. The electron and positron have equal energies $\frac{1}{2}(E_\gamma - 2mc^2)$ and may contribute to the damage of the lattice by the mechanisms listed in Section 2. The positron will annihilate with an electron, producing a further gamma, which will have too low an energy to contribute any more lattice damage. The cross-section for pair production [20] is

$$\sigma_{PP} = \alpha r_0^2 Z_C \left[\frac{28\ln(2\eta)}{9} - \frac{218}{27}\right]. \tag{9}$$

Figure 2 shows the cross-section for the three processes for gamma rays in diamond, showing that Compton scattering dominates throughout the range of energies with

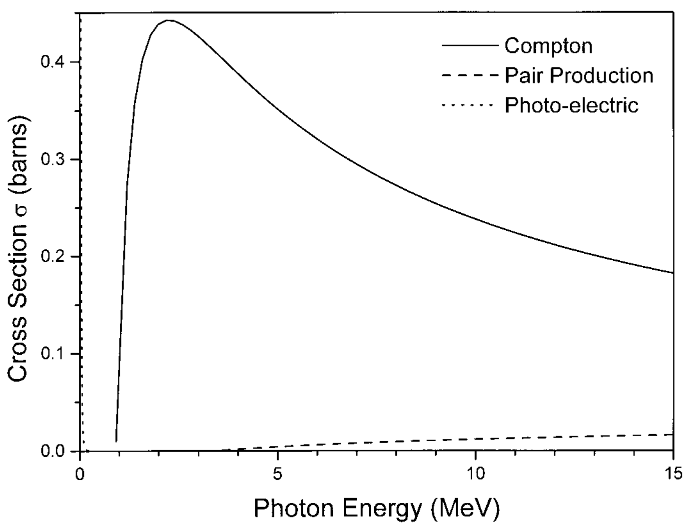

Fig. 2. The cross-sections for gamma ray interaction with diamond by three processes: the photo-electric effect, Compton scattering and pair production

which we are concerned, but pair production is just beginning to become significant at the highest energies. Although the photoelectric effect dominates at energies below 100 keV, the electrons produced do not contribute significantly to the damage of the crystal.

4. Modelling of Radiation Damage in Diamond

4.1 Electron damage

A Monte Carlo programme was written to simulate the progress of incident electrons through diamond. The electron energy, the angle of its path and its depth in the crystal were stored. The electron proceeded in steps of 10 μm, and at each step the electron loss of energy due to ionisation, and the probability of a Rutherford scattering event were calculated. Random numbers were produced to determine whether a lattice atom was displaced, and if so, the energy of the knock-on atom and the depth of the vacancy were stored. The scattering angle of the electron θ was determined by another random number, using the distribution [20]

$$\theta^2 = \frac{4\pi Z_C(Z_C+1)Ne^4(1-\beta^2)}{mc^2\beta^4}\ln\left(\frac{4\pi Z^{4/3}Ne^4(1-\beta^2)x_0}{(\alpha\beta mc^2)^2}\right), \qquad (10)$$

where x_0 is the radiation length in diamond (12.05 cm).

Once the electron had lost so much energy from ionisation and scattering that it could no longer displace atoms, it was considered to have stopped. One million electrons were included to give a smooth distribution of the damage profiles. The data on the knock-on atoms were transferred to TRIM, to calculate the subsequent damage.

4.2 Gamma radiation damage

A similar computer program for gamma irradiation was written. Because the cross-sections for the interaction of gamma rays with carbon are very much smaller than those of electrons, a step length of 100 μm was used. Once an electron was produced by one of the processes described in Section 3, its progress through the crystal was simulated as above and the damage it produced was calculated. Again, the data on knock-on atoms was transferred to TRIM for the further damage to be assessed.

5. Results

5.1 Electron damage

The profiles of total damage have been plotted for three energies of incident electrons (1, 2 and 5 MeV) in Fig. 3. In each case the damage profile has a sharp cut-off. The variation of these maximum depths with energy is plotted in Fig. 4. The total vacancy production for a range of electron energies is shown in Table 1.

5.2 Gamma damage

The gamma rays have a much greater penetration length in diamond than electrons, so we have plotted just the damage profiles in the first 1.5 cm of the diamond, which is greater than the thickness of most diamonds. Figure 5 shows the damage as a function

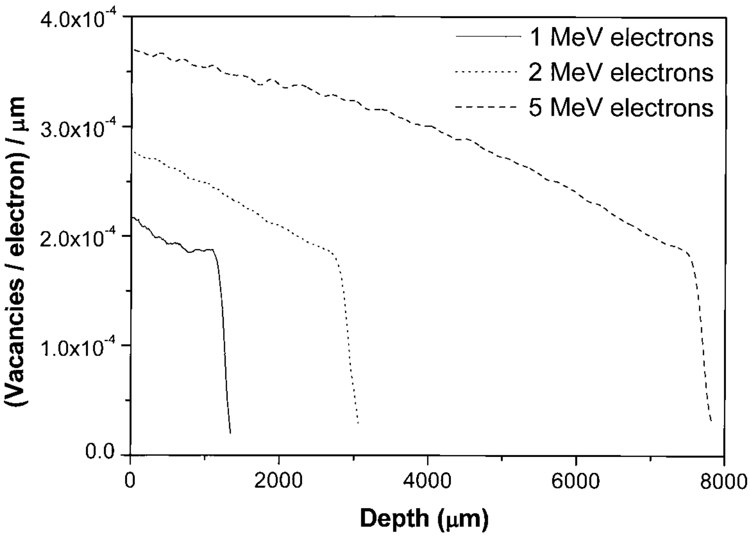

Fig. 3. The number of vacancies per micrometer depth created by 1, 2 and 5 MeV electrons as a function of depth

Table 1
The total vacancies produced per electron

electron energy (MeV)	vacancies/electron	(vacancies/electron)/cm
0.25	0.01	0.74
1	0.23	1.74
2	0.66	2.15 (cf. 1.53 exp. [21])
5	2.23	2.85
10	5.15	3.42

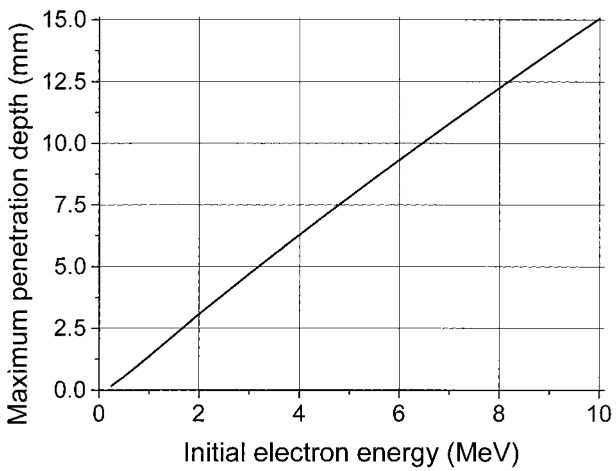

Fig. 4. The maximum penetration depth of electron damage as a function of electron energy

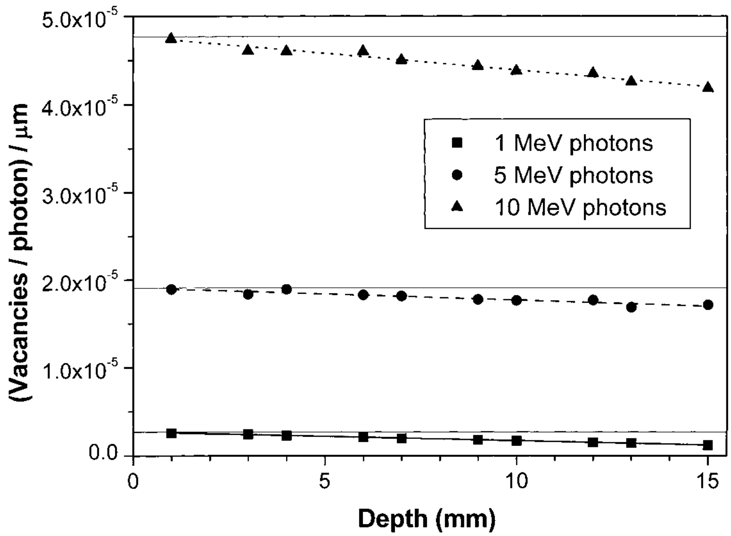

Fig. 5. The vacancies produced per micrometer depth by gamma rays of energy 1, 5 and 10 MeV as a function of depth

of depth: the vacancy production per micrometer is plotted for gamma rays of energies 1, 5 and 10 MeV. The vacancy production per millimeter is shown in Table 2.

6. Annealing of Damage

The atoms displaced by the radiation usually have quite small energies. Therefore they cannot move very far from the vacancy before they come to rest. In fact, for 2 MeV electron damage, TRIM shows that many of the knock-on atoms are displaced less than 5 Å from the vacancy. This raises two concerns: first TRIM is not really valid when the crystal structure and interstitial sites become important on such a small scale, and secondly any atom displaced by less than the distance to the third neighbour of the vacancy is likely to recombine with it. Of course, some of the recombination is already taken into account in the choice of the displacement energy E_d, so the results should be reasonably reliable for low temperature irradiation. At the displacement site, much of the energy is deposited as phonons, which cause a local heating of the diamond. This may allow the interstitials to migrate, even if the nominal irradiation temperature is too low for their normal migration. However, because of the high thermal conductivity of

Table 2
The vacancies produced by gamma irradiation

gamma energy (MeV)	(vacancies/gamma)/cm
1	0.03
2	0.09
5	0.19
10	0.48
15	0.84

diamond, the local heating will dissipate rapidly, and it will only be in the samples irradiated higher than room temperature that the recombination due to local heating near the displacement site causes significant recombination.

We therefore suggest that although these simulations show the damage produced by electrons and gamma radiation at low irradiation temperatures, the damage that *actually survives* is less than this. The comparison with experimental data in Table 1 shows that we over-estimate the production of vacancies by 40%, as expected. We already know that the production of interstitials in diamond is strongly dependent on the temperature of irradiation [21]. More simulations, taking into account this data and the annealing of the interstitial defects, will allow us to complete the radiation damage picture.

7. Conclusions

By taking into account the mechanisms of the interactions of electrons and gamma radiation with matter, we can predict the radiation damage of diamond by these sources. The annealing of the damage is an additional factor reducing the vacancy populations that are detected experimentally.

References

[1] D.R. Kania, M.I. Landstrass, M.A. Plano, L.S. Pan, and S. Han, Diamond Relat. Mater. **5/7**, 1012 (1993).
[2] C. Bauer et al., Nucl. Instrum. Methods A **367**, 207 (1995).
[3] C. Bauer et al., Nucl. Instrum. Methods A **380**, 183 (1996).
[4] M.M. Zoeller et al., IEEE Trans. Nucl. Sci. **44**, 815 (1997).
[5] D. Husson et al., Nucl. Instrum. Methods A **388**, 421 (1997).
[6] P. Weilhammer et al., Nucl. Instrum. Methods A **409**, 264 (1998).
[7] W. Trischuk, Nucl. Instrum. Methods A **419**, 251 (1998).
[8] D. Meier et al., Nucl. Instrum. Methods A **426**, 173 (1999).
[9] E.W.J. Mitchell, in: The Physical Properties of Diamond, Ed. R. Berman, Clarendon Press, Oxford 1965 (p. 364).
[10] G. Davies, Rep. Progr. Phys. **44**, 787 (1981).
G. Davies, S.C. Lawson, A.T. Collins, A. Mainwood, and S.J. Sharp, Phys. Rev. B **46**, 13157 (1992).
[11] D.W. Twitchen, D.C. Hunt, C. Wade, M.E. Newton, J.M. Baker, T.R. Anthony, and W.F. Banholzer, Physica B **273/274**, 644 (1999).
D.C. Hunt, D.W. Twitchen, M.E. Newton, J.M. Baker, T.R. Anthony, and W.F. Banholzer, Phys Rev. B **58**, 1572 (1999).
[12] G.D. Watkins and K.H. Chow, Physica B **273/274**, 7 (1999).
[13] D.W. Palmer, in: Properties and Growth of Diamond, Ed. G. Davies, INSPEC, IEE, London 1994 (p. 143).
[14] A. Mainwood, J. Cunningham, and D. Usher, Mater. Sci. Forum **258/263**, 787 (1997).
[15] F. Seitz and J.S. Koehler, Displacement of Atoms during Irradiation, Solid State Physics, Vol. 2, Academic Press, London/New York 1956 (p. 305).
[16] J. Koike, D.M. Parkin, and T.E. Mitchell, Appl. Phys. Lett. **60**, 1450 (1992).
[17] G.H. Kinchin and R.S. Pease, Rep. Progr. Phys. **18**, 1 (1958).
[18] J.F. Prins, in: The Properties of Natural and Synthetic Diamond, Ed. J.E. Field, Academic Press, London 1992 (p. 301).
[19] J.F. Zeigler, The Stopping and Range of Ions in Solids, A. Wheaton & Co., Oxford 1985.
J.P. Biersack and H.G. Hassmark, Nucl. Instrum. Methods B **174**, 274 (1980).
[20] V.A.J. van Lint, Mechanisms of Radiation Effects in Electronic Materials, Wiley, New York 1980.
[21] D.C. Hunt et al., Phys. Rev. B **61**, 3863 (2000).