On the connection between structural distortion and magnetism in graphene with a single vacancy

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The correlation between structural distortion and emergence of magnetism in graphene containing a single vacancy was investigated using first-principles calculations based on density functional theory (DFT). Our results have shown that a local distortion is formed around the vacancy, with reconstruction of two atomic bonds and with a dangling bond remaining at the third atom adjacent to the vacancy. A systematic investigation of the possible out-of-plane displacement of this third atom was then carried out, in order to ascertain its effects on the magnetic features of the system. The ground state was definitely found to be magnetic and planar, with spin-resolved $\sigma$ and $\pi$ bands contributing to the total magnetic moment. However, we have also found that metastable solutions can be achieved if an initial shift of the third atom above a minimum threshold from the graphene plane is provided, which leads to a non-planar geometry and a non-magnetic state.

I. INTRODUCTION

The issue of magnetism in graphene and related materials-including graphene multilayers, graphite, nanocarbons and others-has been the focus of intense research in the last years, both from the experimental and the theoretical points of view \cite{1,2,7}. The onset of intrinsic magnetic properties is always linked to some kind of defects introduced in the bipartite lattice, such as atomic vacancies, chemisorbed species or edge sites \cite{2,3,6}. Single vacancies cause the appearance of dangling bonds and, depending on the defect concentration and on the degree of passivation associated with eventually present hydrogen atoms, the magnetic moments due to electrons with uncompensated spins in $\sigma$ and $\pi$ orbitals has a trend to vanish at any experimental temperature in defective graphene \cite{8,9}. Some recent calculations performed by Palacios & Ynduráin for variable defect concentrations in graphene sheets containing single vacancies have confirmed these findings, by showing that the vacancy-induced magnetism associated with extended $\pi$ orbitals has a trend to vanish at any experimentally relevant vacancy concentration-thus spoiling any possibility of ferromagnetic or antiferromagnetic interactions associated with those $\pi$ electrons \cite{6}. On the other hand, this work also showed that localized, non-interacting states associated with a flat $\sigma$ band are the only ones surviving for defect concentrations approaching zero, in apparent agreement with the paramagnetic properties experimentally observed for graphene irradiated with protons \cite{10}.

When a single atomic vacancy is formed in an otherwise perfect two-dimensional graphene lattice in the absence of hydrogen (or other gases that could lead to passivation), three dangling bonds remain in the atoms surrounding the vacancy. A Jahn-Teller distortion in this neighborhood leads to the reconstruction of the bond between two of the atoms closest to the vacancy, leaving the third atom less bound to the network and with an unsaturated dangling bond \cite{1,12}, as illustrated in Figure 1. The question then arises whether or not this atom (identified as atom 3 in Figure 1) will remain in the plane, an issue that has received a number of apparently conflicting responses in the last years. El-Barbary et al. used the local density approximation (LDA) in an atomic cluster to model a defective hydrogen-terminated graphene ribbon \cite{13}. They found that the fully optimized structure is distorted, with the atom with the unsaturated dangling bond moving out of the plane by 0.47 Å. When using calculations with spin polarization, the spin-polarized state was found to be higher in energy than the unpolarized one by ca. 0.5 eV, leading the authors to conclude that the ground state of vacancy-containing graphite should be nonmagnetic \cite{13}. A similar method was followed by Dharma-wardana & Zgierski, who used DFT calculations to study the structural, electronic and magnetic properties of a single vacancy in a finite graphene fragment with zig-zag edges terminated with hydrogen atoms \cite{14}. They found the ground state was spin polarized and planar, lying ca. 0.2 eV below the non-planar unpolarized structure, with the latter showing a saddle-like distortion around the vacancy. In contrast, when using periodic boundary conditions to study an infinite graphene sheet containing a single vacancy, no out-of-plane distortions were found in the fully relaxed structure, no matter whether or not spin polarization was used in the calculations \cite{14}. In a related work,
Ma et al., employing the generalized gradient approximation (GGA), concluded that the ground state of graphene containing a single vacancy was spin polarized, with the atom with no reconstructed bonding displaced by 0.18 Å out of the plane \[13\]. When forcing a nonmagnetic solution, which was found to be higher in energy by 0.1 eV as compared to the ground state, they found this displacement being increased to 0.46 Å, in agreement with the results of El-Barbary et al. \[13\]. Accordingly, Dai et al. also found, using the same GGA method, a magnetic moment of 1.33 µB for a monovacancy in graphene and reported an upward shift of atom 3 from the plane by 0.184 Å \[14\]. These results are in contrast with the very recent GGA calculations reported by Nanda et al., who found no displacement of any atom out of the graphene plane containing a single vacancy \[17\].

A more detailed investigation of this issue was reported by Faccio et al., who used GGA calculations to compare the effects caused by carbon vacancies and boron doping in graphene \[15\]. By studying monovacancies in graphene sheets of different sizes (and thus with variable degree of interaction between vacancies in different supercells), these authors found that a nonmagnetic solution was higher in energy by ca. 0.4 eV as compared to the magnetic structure for the whole range of defect concentrations. Also, the establishment of the nonmagnetic solution was accompanied by an out-of-plane displacement of atom 3 by 0.3 Å. Interestingly, it was reported that when this nonmagnetic solution was used as the starting point of a new spin-polarized calculation, allowing full structural relaxation, then the structure relaxed back to the flat graphene sheet, with a net magnetic moment in the range 1.0-1.3 µB, depending on the defect concentration \[18\]. The results recently reported by Ugeda et al. in an investigation about the effects of single vacancies in a graphene monolayer deposited on Pt surface \[19\] also helped to shed some light into this subject. In order to understand the absence of magnetism in the graphene/Pt system, the authors first studied the features of a pure graphene sheet containing a single vacancy; again, spin-polarized calculations showed that the ground state was magnetic (with a magnetic moment of 1.5 µB) and nearly planar, with a nonmagnetic solution found 0.1 eV above the ground state. However, by systematically forcing an out-of-plane displacement of atom 3, a decrease in the magnetic moment as a function of the displacement was obtained, with a nonmagnetic state being found (even using spin-polarized calculations) for a displacement of ca. 0.5 Å. This quenching of magnetic moment was attributed to the mixing of σ and π states in the spin-resolved density of states (DOS), causing a partial or total compensation of the magnetic moments associated with the former σ and π orbitals \[19\]. This conclusion was in agreement with the work by Dharma-wardana & Zgierski, who reported that in the unpolarized structure of a finite graphene fragment with a single vacancy the distortion caused a disconnection of the electron associated with the vacancy from the remaining 2D electron network; this led to the formation of two singlet electron pairs - one associated with the two electrons at atom 3 and the other one associated with the reconstructed bonding between atoms 1 and 2 (see Fig. 1), causing the structure to become nonmagnetic \[14\].

Considering this scenario with some apparently discrepant conclusions as well as a number of sparse complementary findings, we decided to undertake a systematic investigation of the effects of out-of-plane displacements on the structural, electronic and magnetic features of a graphene sheet containing a single vacancy. Both spin-polarized and unpolarized calculations with full structural relaxation were performed, allowing us to compare the total energies, magnetic moments and electronic configurations of each relaxed structure corresponding to different initial displacements. These results unequivocally show that the ground state is indeed planar and magnetic, but the presence of other local energy minima can lead to metastable solutions with different structural and electronic properties.

II. COMPUTATIONAL DETAILS

In this work, we have investigated carbon vacancies in a graphene sheet, through first-principles calculations, based on density functional theory (DFT) \[20\]. The DFT calculations were performed using ultrasoft Vanderbilt pseudopotentials \[21\], and a generalized gradient approximation (GGA) for the exchange-correlation potential \[22\], as implemented in the VASP code \[23–25\]. In order to study the vacancies we have used 6x6 supercell with 72 carbon atoms. The vacancies were created by removing one carbon atom in the graphene sheet. The lattice parameter for graphene obtained from structural optimization was 2.46 Å. We have used a plane-wave-cutoff energy of 400 eV and a Monkhorst-Pack \[26\] scheme with a 5x5x1 k-mesh for the Brillouin zone integration. Calculations were performed both with and without spin polarization for the graphene sheet containing a single vacancy. In all calculations the lattice parameter was kept fixed at the calculated value, whereas the atoms were allowed to relax until the atomic forces were smaller than 0.025 eV/Å.

III. RESULTS AND DISCUSSIONS

Fig. 1 shows the fully relaxed atomic structure of the graphene sheet with a single carbon vacancy, obtained by spin-resolved DFT calculations. This structure clearly shows the local breaking down of the threefold symmetry due to the Jahn-Teller distortion induced by the reconstruction of two dangling bonds left after removing one carbon atom from the graphene sheet. It should be noted that, as a result of this distortion, the atoms 1 and 2 move closer to one another, forming a reconstructed bond with length of 2.07 Å (as compared
to 2.46 Å in defect-free graphene). This gives rise to the in-plane displacements of other carbon atoms in the relaxed structure, as shown in Table I.

**TABLE I:** Distances corresponding to first and second neighbors in a graphene sheet with a single vacancy and in defect-free graphene, where $d_{i,j}$ denotes the distances corresponding to different pairs of atoms as shown in Fig. 1.

| First-neighbors                  | Graphene-vacancy (Å) | Graphene (Å) |
|----------------------------------|----------------------|--------------|
| $d_{1-2} = 2.07$                 | $d_{0} = 1.42$       |
| $d_{7-9} = 2.37$                 |                      |
| $d_{2-8} = d_{8-1} = 2.39$       |                      |
| $d_{5-3} = d_{11-3} = 2.43$      |                      |
| $d_{6-4} = d_{10-12} = 2.44$     |                      |
| $d_{1-3} = d_{2-3} = 2.56$       |                      |
| $d_{2-5} = 2.58$                 |                      |
| $d_{11-1} = 2.59$               |                      |

Table I shows that there exists a variation in the interatomic distances corresponding to second neighbors, ranging from 2.07 Å up to 2.59 Å. The largest change in the in-plane interatomic distances is observed for atoms 1 and 2 ($d_{1-2} = 2.07$ Å) and is associated with the reconstructed bond mentioned above. We can also note that the interatomic distance between first neighbors varies from 1.37 Å up to 1.47 Å, compared to 1.42 Å in defect-free graphene. These results are in good agreement with previous work [7, 16].

The formation energy of a single vacancy in the graphene sheet at the ground state of the system was calculated as

$$E_f = \frac{1}{n}(E_v - \frac{N-n}{N}E_g),$$

(1)

where $N$ denotes the number of C atoms in the defect-free graphene sheet, $n$ represents the number of vacant C atoms (i.e., $n = 1$ in the present case) and $E_g$ and $E_v$ are the total energies of the defect-free and the vacancy-containing graphene sheets, respectively. The formation energy of the graphene sheet containing a single vacancy calculated according to eq. (1) was found to be 7.6 eV, which is in good agreement with the experimental value of 7.0 eV [27] and also with previous results of DFT calculations [16, 18].

In order to verify the existence of possible metastable solutions involving different geometries of the graphene sheet containing a single vacancy, we have investigated in detail the possible displacement of atom 3 (which is the atom that does not form a reconstructed bond with the other ones, indicated by the arrow in Fig. 1) perpendicularly to the sheet. Then, a series of calculations were performed, starting from a structure with atom 3 initially displaced from the sheet by variable distances (named $Z_i$). These calculations were done for both unpolarized and spin-polarized schemes, with the structure being allowed to fully relax. The initial ($Z_i$) and final positions (named $Z_f$ and $Z_f$ for the unpolarized and spin-polarized calculations, respectively) of atom 3 with the corresponding magnetic moments are summarized in Table II whereas the plots of the total energy of the system as a function of the final position reached by atom 3 are shown in Fig. 2.

From the data shown in Table II we can analyze the behavior of the final position reached by atom 3 as a function of its initial position. In the unpolarized case, we can observe that if an initial out-of-plane shift is given to atom 3, then its final position reaches values around 0.42 Å.

**TABLE II:** Final ($Z_f$ and $Z_f$) distances of atom 3 measured from the sheet after full relaxation for unpolarized and spin-polarized calculations, respectively. ($Z'_i$) represents the initial displacement of atom 3 from the graphene sheet and ($\mu$) is the magnetic moment corresponding to the relaxed structure.

| $Z_i$ (Å) | $Z_f$ (Å) | $Z_f$ (Å) | $\mu$ (μB) |
|-----------|-----------|-----------|-------------|
| 0.00      | 0.00      | 0.00      | 1.21        |
| 0.06      | 0.40      | 0.02      | 1.21        |
| 0.08      | 0.40      | 0.05      | 1.20        |
| 0.10      | 0.41      | 0.06      | 1.19        |
| 0.20      | 0.41      | 0.11      | 1.16        |
| 0.30      | 0.41      | 0.13      | 1.12        |
| 0.40      | 0.41      | 0.20      | 1.04        |
| 0.50      | 0.42      | 0.41      | 0.00        |
| 0.60      | 0.42      | 0.41      | 0.00        |
| 0.70      | 0.43      | 0.42      | 0.00        |

FIG. 1: The relaxed atomic structure of the graphene sheet with a single vacancy, where spheres represent the carbons atoms. The arrow indicates the atom 3 with the dangling $\sigma$ bond and atoms 1 and 2 are those rebonded.
Å (even for initial values as small as 0.06 Å). On the other hand, for spin-resolved calculations there exist different metastable solutions that can be reached depending on the initial shift. In particular, it should be noted that for \(Z_f < 0.40 \) Å the final position of atom 3 \(Z_f\) varies from 0.0 up to 0.20 Å, whereas for \(Z_i > 0.40\) the final position is around 0.42 Å, matching the value found in the unpolarized calculations.

Fig. 2 shows how the total energy of each relaxed structure changes as a function of \(Z_f\) or \(Z_f\), for calculations performed without (Figure 2a) or with (Figure 2b) spin polarization, respectively. These results show that the ground state of the relaxed structure is indeed planar (i.e., \(Z = 0\)) and spin-polarized, with a total energy nearly 0.10 eV below that of the unpolarized structure, in good agreement with some previous results [15, 19].

\[\text{Energia (eV)}\]

\[\text{Z_f(Å)}\]

\[\text{Z_i(Å)}\]

FIG. 2: Total energy of the graphene sheet containing a single vacancy calculated as a function of the displacement of atom 3 perpendicular to the sheet (a) without spin polarization and (b) with spin polarization. The lines connecting between the points are guides for the eyes.

As was already mentioned before, the details of the relaxed structure of a graphene sheet containing a single vacancy reported in the literature vary widely. While some authors have reported a planar geometry for the ground state [17, 19], there are also many reports of non-planar structures with out-of-plane displacements varying from 0.18 to 0.47 Å [13, 15, 16]. It is worth emphasizing that in the case of the unpolarized calculations (Figure 2a), atom 3 tends to be shifted by 0.42 Å out-of-plane, whereas the spin-polarized calculations (Figure 2b) yield a planar structure. However, it is interesting to note that even in the case of spin-polarized calculations there exists a clustering of points close to this value of \(Z_f\), suggesting a local energy minimum in this region. This means that if the initial shift of atom 3 is above ca. 0.20 Å, the structural relaxation leads to metastable states with \(Z_f\) around 0.42 Å and with the same total energy as compared to the unpolarized structure (ca. 0.10 eV above the ground state), which can help to understand the reports of shifts with this magnitude found in the literature [15, 16]. Further, it can be observed in Figure 2b that a little energy variation and small differences between \(Z_i\) and \(Z_f\) are detected among the several final structures obtained for \(Z_i\) in the range from 0.00 up to 0.20 Å, which is also consistent with other reports [15, 16]. These results show that the final reached structures are strongly dependent on the use of spin polarization in the calculations [18, 19] and that, even when using spin polarization, the setting of the initial conditions can significantly change the properties of the relaxed structure. It is likely that most of the discrepancies found in the literature regarding the out-of-plane displacements of atom 3 can be associated with the trends illustrated in Fig. 2.

Moreover, the abrupt change of the energy for \(Z_f > 0.20 \) Å can be associated with the reported disconnection of the \(\pi\) electron associated with the vacancy from the 2D electron network [14]. For such large shifts, it is energetically more favorable for the system to accommodate two of the electrons released by the vacancy in a singlet pair at atom 3, with the other two electrons becoming part of the reconstructed \(\sigma\)-like bond between atoms 1 and 2. Thus, this metastable structure must remain nonmagnetic, with the same energy (-650.16 eV) irrespective of the use of spin polarization in the calculations. This behavior can be clearly observed in Figure 3, where the magnetic moment of the graphene sheet containing a single vacancy is plotted as a function of \(Z_f\). It is visible that the planar ground state (\(Z_f = 0.00 \) Å) is magnetic, with a magnetic moment of 1.21 \(\mu_B\); on the other hand, for \(Z_f > 0.20 \) Å the system evolves to a nonmagnetic state, achieved with \(Z_f\) close to 0.42 Å.

\[\text{Magnetic Moment (\(\mu_B\))}\]

\[\text{Z_i(Å)}\]

FIG. 3: Magnetic moment of the graphene sheet containing a single vacancy calculated as a function of the displacement of atom 3 perpendicular to the sheet for the relaxed structure. The line connecting the points is a guide for the eyes.

The changes in the electronic structure related to dif-

This concludes the discussion on the structural and magnetic properties of graphene sheets containing single vacancies, highlighting the importance of spin polarization in predicting the relaxed structure and magnetic moment. Further studies are needed to fully understand the behavior of graphene under various perturbations and conditions.
different atomic configurations as atom 3 is moved away from the graphene sheet are shown in Fig. 4 where we can see the spin resolved band structure for the different \( Z_f \) values, after full relaxation of the system.

![Spin-resolved band structures](image)

**FIG. 4:** Spin-resolved band structures calculated after full relaxation of the graphene sheet containing a single vacancy for three different values of the final displacement of atom 3 perpendicular to the sheet: (a) \( Z_f = 0.00 \text{ Å} \); (b) \( Z_f = 0.20 \text{ Å} \) and (c) \( Z_f = 0.42 \text{ Å} \). The zero of energy is at the Fermi level. Solid and dotted lines represent spin-majority and spin-minority bands, respectively.

The existence of separated spin-minority and spin-majority bands is evident in Fig. 4a and, to a lesser extent, in Fig. 4b, both for \( \sigma \) and \( \pi \) bands, corresponding to \( Z_f = 0.0 \text{ Å} \) and \( 0.20 \text{ Å} \), respectively. With increasing \( Z_f \), one can also observe a broadening of the \( \sigma \) band that was located close to -0.5 eV for \( Z_f = 0 \) and that was associated with a strongly localized state around atom 3 in the planar structure \[1, 19\]. At the same time, the spin-minority \( \pi \) band is pushed down and both \( \pi \) bands are almost completely below the Fermi level for \( Z_f = 0.20 \text{ Å} \), which leads to a reduction in the magnetic moment compared to the planar geometry, as shown in Figure 3. Moreover, Fig. 4c shows that for \( Z_f = 0.42 \text{ Å} \) there exists a complete overlap of spin-majority and spin-minority bands, leading to the quenching of the magnetic moment of the sheet. Then, one can note the \( \sigma \) and \( \pi \) states obtained for \( Z_f < 0.20 \text{Å} \) evolved to \( \sigma^* \) and \( \pi^* \) states, which are combinations of bonding and antibonding orbitals. This leads to a stable electronic configuration with double occupancy of the \( \sigma^* \) state and, partially, of the \( \pi^* \) states, which are now pinned to the Fermi level. The quenching of the magnetic moment of the sheet associated with the out-of-plane displacement of atom 3 has already been previously reported \[19\]. However, it is not clear whether or not a full relaxation of both atomic and electronic coordinates was allowed in the structures reported in ref. \[19\], so it is difficult to quantitatively compare those results with the ones presented here. But the qualitative mechanism describing the quenching of the magnetic moment is clearly consistent with the trends shown in Figs. 2-3 and as atom 3 is shifted away from the graphene plane, there exists a progressive change of hybridization of that atom and a mixture of \( \sigma \) and \( \pi \) states; this changes the occupation of the corresponding spin-majority and spin-minority bands and thus leads to a partial compensation of the spin populations and a reduction in the magnetic moment of the sheet. In the present case, when the displacement of atom 3 exceeds a threshold close to \( Z_f = 0.20 \text{ Å} \), then a complete compensation of spin populations in the now mixed states occurs, leading to the settling of a nonmagnetic state.

**IV. CONCLUSION**

DFT calculations have been employed in a systematic investigation of the effects of out-of-plane atomic displacements on the structural, electronic and magnetic features of a graphene sheet containing a single vacancy. The results showed the occurrence of a local distortion around the vacancy in the relaxed structure, with reconstructed atomic bonds between two atoms close to the vacancy and with the third atom located in the graphene plane. Total energies, magnetic moments and electronic configurations of the final structures reached after full relaxation starting from different initial shifts of this third atom in the direction perpendicular to the graphene sheet were calculated, both for polarized and also for unpolarized structures. The present results showed that the ground state of this system is indeed planar and magnetic, with spin-resolved \( \sigma \) and \( \pi \) bands contributing to the total magnetic moment of the graphene sheet containing a single vacancy. However, we have found the presence of other local energy minima, which can lead to metastable solutions with different structural, electronic and magnetic properties that are strongly dependent on the extent of the out-of-plane shift.

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**references**
[1] Yazyev O V and Helm L, 2007 Phys. Rev. B 75, 125408.
[2] Yazyev O V 2010 Rep. Prog. Phys. 73 056501.
[3] Oeiras R Y, Araújo-Moreira F M and da Silva E Z 2009 Phys. Rev. B 80 073405.
[4] Esquinazi P, Spemann D, Hohne R, Setzer A, Han K-H and Butz T 2003 Phys. Rev. Lett. 91 227201.
[5] Mombru A W, Pardo H, Faccio R, de Lima O F, Leite E R, Zanelatto G, Lanfredi A J C, Cardoso C A and Araújo-Moreira F M 2005 Phys. Rev. B 71 100404(R).
[6] Cervenka J, Katsnelson M I and Flipse C F J 2009 Nature Phys. 5 840-844.
[7] Palacios J J and Yndurain F 2012 Phys. Rev. B 85 245443.
[8] Wang Y, Huang Y, Song Y, X Zhang, Y Ma, J Liang and Chen Y 2009 Nano Lett. 9 220-224.
[9] Ugeda M M, Brihuega I, Guinea F and Gómez-Rodríguez J M 2010 Phys. Rev. Lett. 104 096804.
[10] Nair R R, Sepioni M, Tsai I-L, Lehtinen O, Keinonen J, Krasheninnikov A V, Thomson T, Geim A K and Grigorieva I V 2012 Nature Phys. 8 199-202.
[11] Riccò M, Pontiroli D, Mazzani M, Choucair M, Stride J A and Yazyev O V 2011 Nano Lett. 11 4919-4922.
[12] Faccio R and Mombru A W 2012 J. Phys.: Condens. Matter 24 375304.
[13] El-Barbary A A, Telling R H, Ewels C P, Heggie M I and Briddon P R 2003 Phys. Rev. B 68 144107.
[14] Dharmawardana M W C and Zgierski M Z 2008 Physica E 41 80-83.
[15] Ma Y, Lehtinen P O, Foster A S and Nieminen R M 2004 New J. Phys. 6 68.
[16] Dai X Q, Zhao J H, Xie M H, Tang Y N, Li Y H and Zhao B 2011 Eur. Phys. J. B 80 343-349.
[17] Nanda B R K, Sherafati M, Popovic Z S and Satpathy S 2012 New J. Phys. 14 083004.
[18] Faccio R, Fernández-Werner L, Pardo H, Goyenola C, Ventura O N and Mombrú A W 2010 J. Phys. Chem. C 114 18961-18971.
[19] Ugeda M M, Fernandez-Torre M, Brihuega I, Pou P, Martinez-Galera A J, Pérez R and Gómez-Rodríguez J M 2011 Phys. Rev. Lett. 107 116803.
[20] Hohenberg P and Kohn W 1964 Phys. Rev. 136 864B
Kohn W and Sham L J 1965 Phys. Rev. 140 1133A.
[21] Vanderbilt D 1990 Phys. Rev. B 41 7892-7895.
[22] Perdew J P, Chevary J A, Vosko S H, Jackson K A, Pederson M. R. Singh D J and Fiolhais C, 1992 Phys. Rev. B 46 6671-6687.
[23] Kresse G and Hafner J, 1993 Phys. Rev. B 47 558-561.
[24] Kresse G and Hafner J, 1993 Phys. Rev. B 48 13115-13118.
[25] Kresse G and Furthmüller J, 1996 Comput. Mater. Sci. 6 15.
[26] H.J. Monkhorst and J D Pack, 1976 Phys. Rev. B 13 5188-5192.
[27] P A Thrower, R M Mayer, 1978 Phys. Status Solidi 47 11.