



High-temperature high-pressure annealing of diamond Small-angle X-ray scattering and optical study

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Abstract

Annealing of Ib and IIa diamonds at temperature of 1800°C and pressure of 7.2 GPa was performed. It is shown that for experiments with comparable total duration, the nitrogen aggregation rate is significantly slower for a single-run than for multiple-run annealing. Consequently, many previously reported multiple annealing experiments could overestimate the rate of nitrogen diffusion in diamond. Small-angle X-ray scattering reveals that three-dimensional defect clusters were formed during annealing. The size of clusters (27–57 nm) is similar in annealed natural IaA, IaB, IIa and synthetic Ib diamonds. The presence of clusters is unrelated to ‘platelets’ and contain little, if any, nitrogen. Optical results reveal that annealing resulted in decay of the 4N–2V (H4) defects into 2N–V (H3) and that the B nitrogen defect is not responsible for the N9 optical center. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Many physical and chemical properties of minerals depend on the concentration and type of point and extended defects present in their lattices. Diffusion of point defects can lead to creation of clusters and under favorable conditions even new phases can be formed. In this paper we report on a new type of extended defect formed in diamond during long continuous annealing at high pressure–high temperature (HPHT) conditions.

Oxygen, hydrogen and nitrogen are the principal impurities found in diamond. Nitrogen concentrations can be as high as 0.3 at%. Oxygen and hydrogen

concentrations can be comparable and, in some cases, higher than that of nitrogen. However, while most oxygen and hydrogen atoms reside in internal voids in the diamond lattice and within non-diamond inclusions, nitrogen predominantly forms integral lattice-bonded defects [1].

The common classification scheme for diamond is based on the principal nitrogen defect types as identifiable by infrared (IR) spectroscopy. In type Ib diamond nitrogen is dominantly present as single substitutional atoms, referred to as the C or P1 centers. Most synthetic diamonds belong to this type. HPHT annealing, performed either naturally or under laboratory conditions, leads to aggregation of single substitutional nitrogen atoms to the so-called A and B complexes in the order C → A → B [2–4]. Diamonds with these defects are referred to as type IaA and IaB, respectively. Optical studies [5,6] combined with electron spin resonance

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(ESR) show that the A center is comprised of a pair of nearest-neighbor substitutional nitrogen atoms. The microscopic structure of the B defect is not so firmly established. Results obtained by ESR [7] and optical methods [8] suggest a complex of four nitrogen atoms in tetrahedral coordination around a vacancy.

In addition to these simple point defects, most diamonds are rich in more complex and variable extended defects. Besides dislocations, twins and stacking faults, one of the best-known examples is termed ‘platelets’—planar (in {100} plane) defects containing carbon and nitrogen atoms. It is suggested that platelets are formed from interstitial carbon atoms as a result of their migration at high temperature [9,10]. Another abundant group of extended defects in diamonds is termed ‘voidites’, which are typically octahedral formations with a large scatter in size (1–30 nm) and with lower electron density than diamond. Their composition is uncertain, but N–C–H compounds are considered as probable constituents [11].

X-ray diffuse scattering [12] and high-resolution electron microscopy [13] show that Ia diamonds also contain planar {111} defects. Existence of sphere-like (isometric) clusters with diameter ~ 8 –9 nm [14,15] or larger [16] has been reported. Values for hardness and low-temperature thermal conductivity appear to depend on the presence of such clusters [17]. Extended defects can be produced during laboratory or natural HPHT annealing [3,17].

Recently, large defect clusters have been identified by small-angle X-ray scattering (SAXS) in natural IaB and natural and synthetic IaA diamonds [17]. Measurements reveal the presence of spherical defect clusters about 9 nm in diameter in IaB crystals. In type IaA diamonds, the scattering contrast is much weaker and the cluster sizes are more variable (10–60 nm). The composition of those clusters was not clear, although it has been suggested that they may have a significant nitrogen component [17]. The purpose of this paper is to clarify the composition of large spherical defects (clusters) observed by SAXS by their reproduction under laboratory conditions. We present results of SAXS and optical

measurements on synthetic nitrogen-bearing diamonds and on a natural low-nitrogen stone, annealed at HPHT conditions for different periods, and demonstrate that nitrogen, if present at all, is not a significant part of those clusters.

In laboratory experiments on nitrogen aggregation, diamonds are usually annealed in a sequence of several short runs at high temperatures (up to 2800°C) in order to increase diffusion rate. Mechanical stresses as well as changes in pressure–temperature parameters during conventional annealing experiments unavoidably influence defect diffusion. The situation is very different for the majority of natural diamonds, which are annealed at relatively stable upper mantle conditions, at modest temperatures ($< 1400^\circ\text{C}$ [18]), but for time-scales of $\sim 10^9$ years. Therefore, in the present work we performed experimental runs with durations up to 960 h hoping to make a closer approximation to the conditions of annealing of diamonds in the Earth’s mantle.

2. Experimental

Two synthetic nitrogenous Ib diamonds and one low-nitrogen (IIa) natural stone from the Juina district of Brazil have been used in this work. Synthetic diamonds were grown with a Ni-based catalyst. Nitrogen contents in them, determined by Fourier-transform IR spectroscopy (FTIR), are presented in Table 1. Nickel content of synthetic stones was measured using synchrotron-based X-ray fluorescence (beamline L, HASYLAB). Total Ni concentration was of the order of tens of atomic ppm. Optical measurements, discussed below, revealed that the concentration of Ni-related point defects was on the ppb level, and thus most of Ni was likely present as metallic inclusions. FTIR measurements of the type IIa stone showed a presence of < 20 ppm of nitrogen and no Ni could be detected in it by optical absorption or luminescence.

HPHT experiments were carried out using the Walker-style 1000-ton multi-anvil press of the Lunar

Table 1
Defect parameters in annealed diamond samples

Sample number	Nitrogen type	Duration (h)	Total N content (at. ppm)	Nitrogen aggregation ^a (%)	SAXS cluster size (nm)
1 ^b	Ib	10 h 40'	250	25	57
2	Ib	10	240	7	57
3	Ib	100	250	14	44
4	Ib	960	255	10	44
5	IIa	100	20	—	27

^aNitrogen aggregation is a ratio of A center concentration to the total nitrogen content after annealing. It was below 1% before annealing.

^bSample 1 was annealed incrementally in five separate experiments run for 462, 2, 74, 76 and 25 min.

and Planetary Laboratory, University of Arizona. Runs were conducted at 7.2 GPa and $\sim 1800^\circ\text{C}$ using 14/8 mm assemblies. Durations ranged from 10 h to 40 days and are provided in Table 1. Diamond fragments of approximately 2 mm in maximum dimension were loaded into Pt capsules and packed with dry graphite. Pressures of 7.2 GPa were obtained at a ram force of 294 tons (US) following calibration by Righter and Drake [19] and are believed to approximate well to hydrostatic conditions. Temperatures were held at 1595°C as measured directly using $\text{WRe}_{26}/\text{WRe}_5$ thermocouples located on the edge of the heater, 2.0 mm from the hot spot where the diamonds were located. Equivalent power, which was found to be a reliable estimation of temperature, was held constant for experiments where thermocouples failed. Measurements using a similar assembly with the thermocouple located at the hot spot confirm a temperature gradient of $\sim 100^\circ\text{C}/\text{mm}$, and thus samples are concluded to have been subjected to temperatures of $1795 \pm 50^\circ\text{C}$. Experiments were quenched by disconnecting the power supply.

SAXS measurements were performed in the angular region of $15' - 1.2^\circ$. A small-angle AMUR-K X-ray diffractometer [20] with Kratki-collimator and linear position-sensitive detector were used with a Ni-monochromated Cu-anode X-ray fine focus tube as the source of X-rays. The experimental curves were normalized to the primary beam intensity by applying corrections for sample absorption coefficients and holder scattering. Calculation of the size distribution of scattering objects was performed using GNOM software [21]. All mean defect diameters reported in this study are obtained from solutions, stable against variations of a maximum size of scattering centers. The best agreement with the experimental data was achieved by approximation of scattering centers as a polydisperse system of hard spheres.

FTIR spectra were acquired with a Philips PU9800 spectrometer in the range $400 - 3500 \text{ cm}^{-1}$ at a 2 cm^{-1} resolution. Deconvolution of spectra was performed using software provided by David Fisher (D.T.C.). Most samples cracked during the annealing and thus the IR spectra of treated samples were taken from irregularly shaped pieces. Instead of conventional transmission geometry, a superposition of transmitted and diffuse components was measured using a DRIFT sample holder. This could affect the analysis of IR spectra. However, no significant changes in total nitrogen content with annealing were observed in IR spectrum from any sample.

Optical absorption was measured in the range 1.2–5.6 eV at 77 and 300 K using a home-built spectrometer. For given sample thickness a sensitivity of $\sim 10^{-2} \text{ cm}^{-1}$ was achieved. Photoluminescence (PL) measurements were performed at 77 and 300 K under 3.68 eV or 2.41 eV excitation provided by N_2 or Ar^+ lasers,

respectively. For 2.41 eV excitation the spectra could be measured at energies above (anti-Stokes mode) and below (normal, Stokes mode) the excitation laser line. This allowed interference-free detection of the H3 system with a zero-phonon line at 2.463 eV under 2.41 eV excitation. PL spectra were scaled to the integrated diamond Raman peak. After normalization, the concentration of the detected PL centers could be estimated by comparison of the spectra with the standards, in which the concentration of those centers was calibrated by optical absorption using the data of Davies [8].

3. Results

3.1. Optical studies

Optical spectra measured on the Ib HPHT samples before annealing were rather featureless: Absorption measurements revealed only a broad spectrum, associated with the C centers and only the 2.56 eV system, attributed to the Ni_i^- defect [8], has been observed in PL. Luminescence intensity was relatively weak, suggesting that the corresponding defect is present on the ppb level. The PL intensity was the same in samples 1 and 2 being about 3 times stronger than in the samples 3 and 4. Only C-defect spectra were detected in IR absorption, which were used to deduce the nitrogen content in the samples (see Table 1).

After annealing the intensity of the C center absorption decreased and a threshold at 4 eV, associated with the A center, emerged in all Ib samples. The signature of this center was also seen in IR absorption spectra. Moreover, weak absorption appeared from the 1.945 eV system, which was associated with the negatively charged nitrogen–vacancy ($[\text{N}-\text{V}]^-$) complex [8]. By integrating the corresponding vibronic band the $[\text{N}-\text{V}]^-$ concentrations were inferred as 80, 80, 120 and 170 ppb with the uncertainty of 40% for samples 1, 2, 3 and 4, respectively. PL from all these samples became much brighter after annealing. Spectra under 3.68 eV excitation from the Ib HPHT samples 1 and 2 were dominated by the S2 and S3 systems, associated with different complexes involving one Ni and two or more nitrogen atoms [22]. Intensity of PL was the strongest in sample 1, an order of magnitude weaker in sample 2 and even more faint in samples 3 and 4. In accordance with the absorption results, PL spectra under 2.41 eV excitation revealed the 1.945 eV system, having about the same intensity in samples 1 and 2 and about twice as strong in samples 3 and 4. However, sample 1 in addition showed the H3 system with intensity comparable to that of the $[\text{N}-\text{V}]^-$ band. Meanwhile, the H3 luminescence was much weaker in sample 2 and undetectable in samples 3 and 4.

Along with the UV-visible absorption and PL results, IR measurements on annealed samples show that the degree of nitrogen aggregation decreases from sample 1 to 4. Along with the absorption, related to the A defect, a weak E-component appeared. This component has been previously reported in some natural Ia/Ib diamonds [23].

In type IIa diamond (#5) optical absorption measurements reveal a presence of the N9 center on the level ≤ 1 ppm. PL detected minute amounts (ppb level) of N3 as well as H3, H4, 536 nm and 576 nm centers. Analysis of the vibronic structure revealed that the 576 nm system is irrelevant to the 575-nm $[N-V]^0$ related center. Annealing did not produce any changes in the intensity of N9, N3, 536 nm and 576 nm systems. Meanwhile, the intensity of the H4 lines decreased while that of the H3 signals increased. Comparison of absorption spectra from the different pieces of sample 5, before and after annealing, with absorption spectra from natural IaB diamonds revealed that no correlation exists between the intensity of N9 absorption and the concentration of nitrogen in the B form. For example, strong N9 peaks were recorded in the IIa sample 5 with almost no (≤ 20 ppm) B defects. Along with the previous work [24] this result disproves a widely tolerated idea that the N9 center is related to the B nitrogen.

No platelets were observed in IR spectra of our samples either before or after annealing.

Comparison of optical results of each run shows that, unexpectedly, the aggregation of nitrogen was the highest in sample 1, which was annealed for only 10 h but in several steps (see Table 1). All samples, but #5, still contain an appreciable fraction of nitrogen in the C form after annealing and only a small fraction ($\leq 25\%$) of nitrogen converted to pairs (A defect). This result is at odds with many other works, where almost complete transformation of nitrogen (C \rightarrow A) could be achieved after few hours of annealing at similar conditions [2–4].

3.2. Small angle X-ray studies

An introduction to the theory and details of the SAXS technique can be found in Ref. [25]. All diamonds investigated in this work were examined by SAXS and showed no scattering prior to the annealing. This indicates the absence of defect clusters.

After 100 h or 960 h annealing of synthetic stones (3 and 4) SAXS signals appeared. The deduced gyration radius of scattering defects was rather close for both samples and is equal to 17 nm. The best agreement with the experimental curves was achieved using the hard sphere approximation. The diameter of the spherical defects in samples 3 and 4 were estimated as 44 nm. Despite the similarity of defects size in samples 1–4 the scattering in sample 4 was much more intense than in samples 1–3. This indicates a higher contrast of

electronic density of the clusters with the diamond matrix and/or higher concentration of clusters per unit volume of diamond.

Rather unexpectedly, strong scattering, comparable to that from sample 4, was observed in the annealed type IIa diamond (sample 5). The diameter of defects in it is, however, significantly smaller and is close to 27 nm. The difference between SAXS curves prior and after annealing is shown in Fig. 1.

After 10 h annealing of synthetic diamonds (both incremental and continuous, samples 1 and 2) SAXS curves were close to the background. Because the approximation of defects by the hard spheres satisfactorily fitted experimental curves from samples 3, 4 and 5 this model was also applied to the small signals in samples 1 and 2 and yielded a diameter of the spherical defects of ~ 57 nm. However, referring to the weakness of the experimental signals, we would stress the approximate nature of this result.

The sizes of defects responsible for SAXS in samples studied in this work are similar to those observed previously for annealed synthetic and natural IaA diamonds [17]. Our SAXS data show that there is no well-defined boundary between the defect and surrounding matrix. Similar results were obtained earlier from X-ray diffuse scattering [26].

One of the most important results of this study is that the contrast between scattering clusters and the diamond matrix as well as their size can be similar in nitrogen-rich and nitrogen-poor samples. The contrast between the electronic density of the defects and the diamond matrix is significant. For nitrogen-containing samples this contrast increases with the duration of annealing and the defects size possibly decreases with the annealing time, though the latter fact needs larger statistics. Significant changes in the X-ray scattering became observable in the IIa (low-nitrogen) diamond after much shorter annealing (100 h), than that for the nitrogen-containing sample #4 (960 h). However, the reason for this phenomenon could be that the IIa

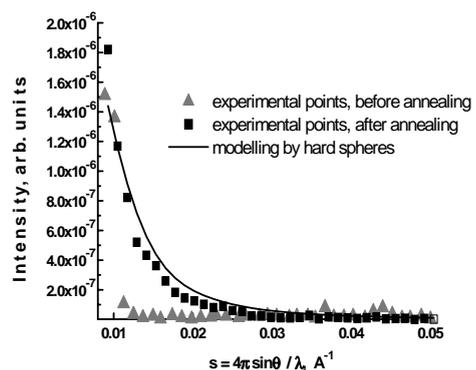


Fig. 1. Small-angle scattering from type IIa natural diamond.

diamond used in our study was natural and thus already significantly annealed. This explanation is supported by the fact that the small amount of nitrogen (<20 ppm) in this sample was present in the aggregated B form already before the experiment.

4. Discussion

Several factors can account for the observed small degrees of nitrogen aggregation and the differences between continuous and incremental runs. It is known that atoms of transition metals strongly increase nitrogen aggregation rate [27]. According to PL measurements, the concentration of Ni atoms was lowest in samples 3 and 4 which, combined with the longer durations of these experiments could explain the low aggregation rate observed for these samples compared to 1 and 2. However an additional mechanism is required to account for the differences in aggregation rate between samples 1 and 2 which contain the same quantities of nickel. During every HPHT annealing cycle some non-hydrostatic pressure component is present, especially when pressurizing and depressurizing the sample. This can result in production of vacancies, thus greatly facilitating nitrogen diffusion [28]. With annealing time, the majority of vacancies should disappear into a variety of sinks, and diffusion rates should subsequently decrease unless a new pressure load-release cycle occurs. We would conclude from these observations that many historical experiments on nitrogen aggregation could produce artificially high diffusion rates compared to natural settings which do not involve cyclical pressure changes.

One of the major results of this study is that continuous annealing leads to much lower nitrogen aggregation rate, than a series of short runs of comparable total duration. This should be taken into account when analyzing results of experiments on nitrogen aggregation.

Our experimental results also suggest that the observations by SAXS isometric clusters in diamond are not related [17] to previously reported extended defects in diamond, such as platelets or voidites. To the best of our knowledge, neither platelets nor voidites have ever been observed in IIa diamonds, whereas we have been able to produce the clusters in diamonds of that type. Additionally, the presence of defect clusters, differing from platelets, is indirectly supported by positron annihilation measurements [29,30]. The contrast of electronic density with the diamond matrix is much higher for platelets than for the clusters we observe, and additionally, the cluster contrast is sample dependent. It is reasonable to suggest that the variations of contrast could be related to different amounts of point defects inside the cluster. For example, pressure

increases the rate of interstitial-assisted diffusion [31]. If the clusters contain appreciable amount of interstitial atoms, then their contrast with the diamond matrix may depend on pressure during annealing. Pressure used in our experiments (7.2 GPa) is higher than average pressure experienced by most natural diamonds (4–5 GPa [18]). This could be an explanation why the SAXS contrast is higher for experimentally annealed samples than for natural IaB diamonds.

The similarity of SAXS patterns in annealed Ia and IIa diamonds does not obviate the possibility of nitrogen as a component of all clusters per se. For example, it was shown that ‘man-made’ voidites [32] and platelets [33] differ from ‘natural’ ones in terms of size, shape and probably, composition. Similarly there could be a large variety of ways to form observed extended defects. In several papers voidites formation was correlated with the platelet degradation [11,32], however, voidites have also been reported for diamonds without platelets or dislocation loops [34]. Despite the size differences, there is no evidence from SAXS measurements to suggest that the clusters in nitrogen-rich Ia and nitrogen-free IIa diamonds have different compositions. It is concluded therefore, that the clusters, observed in the present experiments, in addition to those observed previously for IaA and IaB stones [17], do not consist of nitrogen, but possibly contain carbon interstitials.

5. Conclusions

Annealing of Ib and IIa diamonds at temperature of ~1800°C and pressure of 7.2 GPa was performed. Long continuous runs (up to 40 days) were used in order to simulate the conditions of the upper mantle of the Earth and spectra obtained are similar to naturally annealed diamonds. It is shown that the nitrogen aggregation rate is significantly slower in single duration experiments than in those involving several runs, despite similar total time. It is therefore considered likely that many multiple-run annealing experiments described in literature over-estimate the rate of nitrogen diffusion in diamond. This conclusion has a significant bearing on the age/temperature relationships calculated for natural diamonds.

Three-dimensional clusters of defects were formed during our experiments, as detected by SAXS. Their size is similar to that of clusters previously observed in annealed natural and synthetic IaA and IaB diamonds. Nitrogen, if present at all, is not an important component of these clusters, but they may contain carbon interstitials. Generation of the observed clusters is independent of the formation of platelets.

Optical results reveal that HPHT annealing can lead to decay of the 4N–2V (H4) defects into 2N–V (H3) and that the N9 optical center is not the B nitrogen defect.

References

- [1] J.P.F. Sellschop, Nuclear probes, in: J.E. Field (Ed.), *The Properties of Diamond*, Academic Press, London, 1992.
- [2] R.M. Chrenko, R.E. Tuft, H.M. Strong, *Nature* 290 (1977) 40.
- [3] T. Evans, Z. Qi, *Proc. Roy. Soc. London A* 381 (1982) 159.
- [4] Yu.A. Klyuev, A.M. Naletov, V.I. Nepsha, L.D. Belimenko, V.A. Laptev, M.I. Samoilovich, *Russ. J. Phys. Chem.* 56 (1982) 323.
- [5] E.V. Sobolev, N.D. Samsonenko, V.E. Il'in, *J. Struct. Chem.* 10 (1969) 552.
- [6] G. Davies, *J. Phys. C* 9 (1976) L537.
- [7] J.A. van Wyk, G.S. Woods, *J. Phys.: Condens. Matter* 7 (1995) 5901.
- [8] G. Davies, *Physica B* 273–274 (1999) 15.
- [9] J.M. Baker, *Diam. Rel. Mater.* 7 (1998) 1282.
- [10] J.P. Goss, B.J. Coomer, R. Jones, T.D. Shaw, P.R. Briddon, S. Oberg, *Diam. Rel. Mater.* 10 (2001) 434.
- [11] P.B. Hirsch, P. Pirouz, J.C. Barry, *Proc. Roy. Soc. London A* 407 (1986) 168.
- [12] V.I. Lisoivan, *Fiz Tverdogo Tela* 21 (1979) 240 (in Russian).
- [13] J.C. Walmsley, A.R. Lang, M.-L.T. Rooney, C.M. Welbourn, *Philos. Mag. Lett.* 55 (1987) 209.
- [14] Yu.A. Klyuev, A.M. Naletov, V.I. Nepsha, N.I. Epishina, T.A. Buligina, *Sov. Phys. Solid State* 19 (1977) 7.
- [15] A.M. Naletov, Yu.A. Klyuev, V.I. Nepsha, T.A. Buligina, N.I. Epishina, *Fiz. Tverdogo Tela* 19 (1977) 1529 (in Russian).
- [16] R.R. Ramanan, S.N.N. Goswami, K. Lal, *Acta Crystallogr. A* 54 (1998) 163.
- [17] A.A. Shiryaev, Yu.A. Klyuev, A.M. Naletov, A.T. Dembo, B.N. Feigelson, *Diam. Relat. Mater.* 9 (2000) 1494.
- [18] G.P. Bulanova, *J. Geochem. Explor.* 53 (1995) 1.
- [19] K. Righter, M.J. Drake, *Earth Planet. Sci. Lett.* 173 (1999) 361.
- [20] L.Yu. Mogilevsky, A.T. Dembo, D.I. Svergun, L.A. Feigin, *Kristallografia* 29 (1984) 581 (in Russian).
- [21] D.I. Svergun, *J. Appl. Crystallogr.* 25 (1992) 495.
- [22] V.A. Nadolnny, A.P. Yelisseyev, O.P. Yuryeva, B.N. Feigelson, *Appl. Magn. Res.* 12 (1997) 543.
- [23] C.D. Clark, S.T. Davey, *J. Phys. C* 17 (1984) 1127.
- [24] G. Davies, I. Summersgill, *Diam. Res.* 1 (1973) 6.
- [25] L.A. Feigin, D.I. Svergun, *Structure Analysis by Small-Angle X-ray and Neutron Scattering*, Plenum Press, New York, 1987.
- [26] A.M. Naletov, Ph.D. Thesis, Kiev, 1978 (unpublished).
- [27] I. Kiflawi, H. Kanda, D. Fisher, S.C. Lawson, *Diam. Rel. Mater.* 6 (1997) 1643.
- [28] A.T. Collins, *J. Phys. C* 11 (1978) L417.
- [29] A.A. Shiryaev, A. van Veen, H. Schut, A.C. Kruseman, O.D. Zakharchenko, *Radiat. Phys. Chem.* 58 (2000) 625.
- [30] A.A. Shiryaev, K. Iakoubovskii, A. van Veen, H. Schut, R. Escobar Galindo, O.D. Zakharchenko, Yu.A. Klyuev, F.V. Kaminsky, B.N. Feigelson, *Mater. Sci. Forum* 363–365 (2001) 40–46.
- [31] M. Aziz, *Appl. Phys. Lett.* 70 (1997) 2810.
- [32] T. Evans, I. Kiflawi, W. Lyuten, G. van Tendeloo, G.S. Woods, *Proc. Roy. Soc. London A* 449 (1995) 295–313.
- [33] I. Kiflawi, J. Bruley, W. Lyuten, G. van Tendeloo, *Philos. Mag. B* 78 (1998) 299.
- [34] G. van Tendeloo, W. Luyten, G.S. Woods, *Philos. Mag. Lett.* 61 (1990) 343.