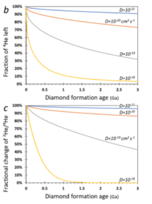
Lattice location of implanted ^{6}He in diamond

U. Wahl[1], J.G. Correia[1], A.R.G. Costa[1], B. Biesmans[2], G. Magchiels[2], S.M. Tunhuma[2], A. Vantomme[2], and L.M.C. Pereira[2]

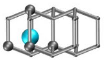
1 Centro de Ciências e Tecnologias Nucleares, Instituto Superior Técnico, Universidade de Lisboa, Portugal
2 KU Leuven, Quantum Solid State Physics, Leuven, Belgium

Motivation:

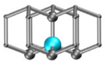
- One of the major scientific interests in the behaviour of He in diamond is due to the belief that the amount of ^{4}He and the ^{3}He/^{4}He ratio found within the material or its inclusions can be used to date terrestrial diamonds [1,2] or learn about the origins of meteoritic nanodiamonds [3].
- Recently, He implantation has also been found to create colour centers in diamond that act as single photon emitters [4].
- Among the issues of interest are the **lattice location of He**, which also concerns the one following ion implantation, since e.g. part of ^{4}He is introduced into the material due to the alpha decay from the $^{235+238}$U and ^{232}Th decay chains, as well as its **diffusion behaviour**, which is responsible for loss of He due to out-diffusion.
- Theory has predicted tetrahedral interstitial T sites to be the preferred positions of He in Diamond [5-8].
- Theoretical predictions for the activation energy for interstitial migration of He are 2.35 eV [5], 1.97 eV [6], and 1.41 eV [9].
- Emission channeling lattice location experiments at CERN-ISOLDE are uniquely suited to study the structure of ion-implanted He in diamond.



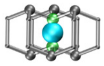
Model predictions for change of ^{4}He and ^{3}He / ^{4}He with diamond age for various assumptions of He diffusivities. ^{3}He / ^{4}He ratios change because ^{3}He is not produced by $^{235+238}$U and ^{232}Th decay chains. From [2].



Tetrahedral (T) interstitial He



Substitutional (S) He



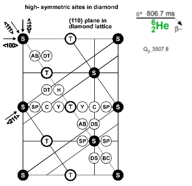
He in split-vacancy configuration (BC)

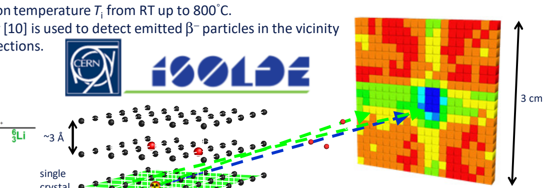
Defect geometries for He in diamond considered in most theoretical studies. From [8].

[1] S. Basu, et al, "An overview of noble gas (He, Ne, Ar, Xe) contents and isotope signals in terrestrial diamond", Earth-Science Reviews 126 (2013) 235.
[2] Y. Weiss, et al, "Helium in diamonds unravels over a billion years of craton metasomatism", Nature Comm. 12 (2021) 2667.
[3] A.P. Koscheev, et al, "History of trace gases in presolar diamonds inferred from ion-implantation experiments", Nature 412 (2001) 615.
[4] [4] G. Prestopino, et al, "Photo-physical properties of He-related color centers in diamond", Appl. Phys. Lett. 111 (2017) 111105.
[5] [5] J.P. Goss, et al, "Density functional simulations of noble-gas impurities in diamond", Phys. Rev. B 80 (2009) 085204.
[6] D.J. Cherniak, et al, "Diffusion of He, H and D in diamond: Experiment, theory and geochemical applications", Geochimica et Cosmochimica Acta 232 (2018) 206.
[7] A. Aghajamali, et al, "Molecular Dynamics Approach for Predicting Release Temperatures of Noble Gases in Presolar Nanodiamonds", Astrophys. J. 916 (2021) 85.
[8] R.A. Beck, et al, "Electronic Structures and Spectroscopic Signatures of Noble-Gas-Doped Nanodiamonds", ACS Phys. Chem. Au 3 (2023) 299.
[9] R. Granot, R. Baer, "Can primordial helium survive in diamonds on geologic time scales?", https://www.researchgate.net/publication/238116629, unpublished (2015).

Emission Channeling with Short-Lived Isotopes (EC-SLI)

- Radioactive ^{6}He ($t_{1/2}$=806.7 ms) isotopes are produced at CERN-ISOLDE and implanted (30 keV) into a CVD diamond single crystal (Element 6, SC plate, [N]<1 ppm) varying the implantation temperature T_i from RT up to 800˚C.
- A position-sensitive detector [10] is used to detect emitted β⁻ particles in the vicinity of major crystallographic directions.

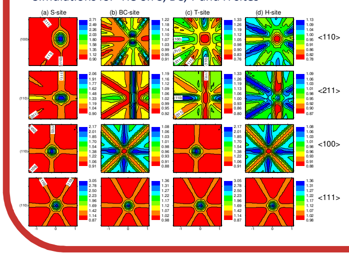




3x3 cm² Si pad detector [7]
22x22 pixels of 1.3x1.3 mm²
max. ~5 kHz

[10] U. Wahl *et al*, "Position-sensitive Si pad detectors for electron emission channeling experiments", Nucl. Instr. Meth. A 524 (2004) 245.

Simulations for ^{6}He on S, BC, T and H sites

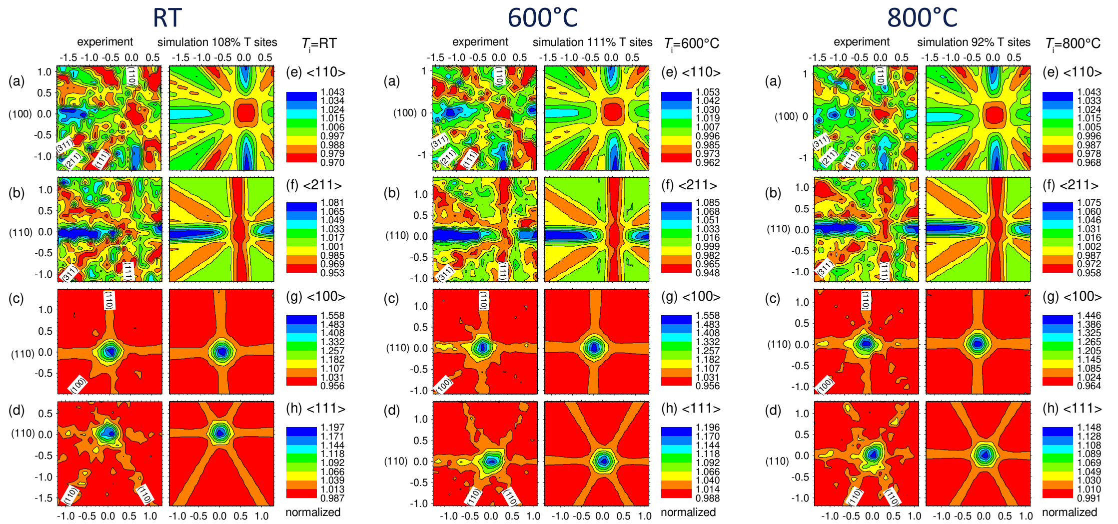


- Depending on the lattice site of the ^{6}He atoms, emitted β⁻ particles are channeled or blocked on their way out of the crystal.
- Substitutional: channeling
  ⇒ yield enhancement
- Interstitial: blocking
  ⇒ yield reduction

- Angular dependent β⁻ emission patterns characterize the lattice site distribution of the ^{6}He emitter atoms.
- Theoretical patterns for different ^{6}He lattice sites calculated using the "many-beam" approach [11]

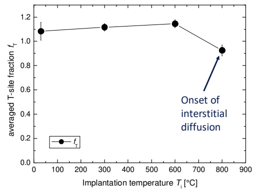
[11] H. Hofsäss, G. Lindner, "Emission channeling and blocking", Physics Reports 201 (1991) 121.

EC results and best fits of simulated patterns



- General features of angular emission patterns: **channeling** along <100> and <111> axes, (100), (110) and (211) planes, **blocking** along <110> and <211> axes, (111) and (311) planes
- **These features are consistent with occupation of tetrahedral interstitial T sites.**
- Detailed analysis by means of fitting theoretical patterns gives the following results:
- T_i =RT=30˚C: 108% T sites
- T_i =600˚C: 111% T sites
- T_i =800˚C: 92% T sites
- No other sites could be identified.
- Fitted fraction values above 100% indicate an inaccurate attribution of gamma and electron backscattering background. Estimated systematic error: ±10% (constant for all measurements, thus does not explain changes with temperature).

^{6}He on T sites as function of implantation temperature



- Fraction of ^{6}He on T sites stable up to 600˚C, then showing a 20% drop at 800˚C.
- Possible reason for the drop: ^{6}He starts to diffuse interstitially and is able to reach the surface of the sample or disappear into the bulk.
- Under these assumptions, we can estimate the activation energy for interstitial migration of ^{6}He as follows to be E_M =1.73 eV:

The diffusivity D of He is given by $D = D_0 \exp\left[-\frac{E_M}{kT}\right]$

With the entropy constant D_0 $D_0 = l^2 \nu_0 N_{NN}$ l… interstitial jump width, ν_0… jump attempt frequency
N_{NN}… number of available jump sites

The mean diffusion width R is given by $R = \sqrt{D\tau}$ τ… radioactive lifetime of ^{6}He

Taking the mean diffusion width R equal to the implantation depth R=1375 Å, we solve for E_M:

$$E_M = -kT \ln\left[\frac{D_0 \tau}{R^2}\right] = -kT \ln\left[\frac{l^2 \nu_0 N_{NN} \tau}{R^2}\right]$$

With τ=1.164 s, l=1.545 Å, N_{NN} =4, ν_0 =2.39×10^{13} s^{-1}[6], T=1073 K, this yields E_M =1.73 eV.

Conclusions

- **The vast majority (if not all) of implanted He in diamond is found on tetrahedral interstitial T sites in accordance with theoretical predictions [5-8]. Possible other lattice sites could not be identified and must be at maximum a few percent only.**
- **The activation energy E_M for interstitial migration of He in diamond suggested from our study is 1.73 eV, which is in reasonable agreement with theoretical predictions of E_M=2.35 eV [5], 1.97 eV [6], and 1.41 eV [9].**

⇒ **Activation energies around 2 eV result in such high interstitial diffusivities (>6×10^{-11} cm^{2}s^{-1}) at earth mantle temperatures (~900-1400˚C) that simple interstitial He in diamond cannot be stable on geological time scales of 10^9 years. The high pressure inside the mantle (up to 20 GPa) is suggested to lower E_M to 1.2 eV [9], so that diffusivities supposedly may even be considerably higher.**

⇒ **To remain inside the diamond, He must be bound to defects in the material or exist in another form such as within inclusions of other minerals or liquids [2], possibly small He bubbles [9] or platelets [12].**

- These experiments are part of a systematic, wider study which also investigates other noble gas isotopes like ^{23}Ne (37 s), ^{87}Kr (76 min), ^{133}Xe (5.2 d), ^{135}Xe (9.1 h).

[12] W. Lin, et al, "Creating two-dimensional solid helium via diamond lattice confinement", Nature Comm. 13 (2022) 5990.

- **Acknowledgements:**
- ISOLDE Collaboration and technical teams
- Research Foundation-Flanders (FWO)
- Portuguese Foundation for Science and Technology (FCT, CERN/FIS-TEC/0003/2021, UID/Multi/04349/2019)
- KU Leuven
- EU Horizon Europe Framework supported ISOLDE beam times through grant agreement 101057511 (EURO-LABS)