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Diamond and its olivine inclusions: a strange relation revealed by ab initio simulations

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Abstract

The study of diamond and its solid inclusions is of paramount importance to acquire direct information on the deepest regions of the Earth. However, although diamond is one of the most studied materials in geology, the diamond-inclusion relationships are not yet understood: do they form simultaneously (syngenesis) or are inclusions pre-existing objects on which diamond nucleated (protogenesis)?

Here we report, for the first time, adhesion energies between diamond (D) and forsterite (Fo) to provide a crucial contribution to the syngenesis/protogenesis debate. The following interfaces were investigated at quantum-mechanical level: (i) $(001)_D/(001)_{Fo}$, (ii) $(001)_D/(021)_{Fo}$, and (iii) $(111)_D/(001)_{Fo}$. Our data, along with the ones recently obtained on the $(110)_D/(101)_{Fo}$ interface, revealed an unexpected thermodynamic behaviour, all interfaces showing almost equal and low adhesion energies: accordingly, diamond and olivine have an extremely low chemical affinity and cannot develop preferential orientations, even during an eventual epitaxial growth. Combining these

results with those of our previous work concerning the morphology constraints of diamond on its inclusions, we can state that the two main arguments used so far in favour of diamond/inclusions syngenesis cannot be longer considered valid, at least for olivine.

Key words: diamond, olivine inclusion, epitaxy, syngenesis, protogenesis

1. Introduction

The characterization of mineral inclusions in diamond (D) allowed to indirectly obtain information about the genesis and distribution of diamonds in the Earth's mantle (e.g., Pearson et al., 2014; Shirey et al., 2013; Stachel and Harris, 2008). Such inclusions have been classified, according to the timing of their formation with respect to the host diamond (Meyer, 1987; Harris, 1968a, 1968b), as: (i) *syngenetic*: when they form simultaneously with the diamond; then, syngenesis implies either inclusion/host mutual growth through co-precipitation from the same medium or complete recrystallization of a pre-existing mineral occurring when diamond grows; (ii) *protogenetic*: when they represent pre-existing minerals passively incorporated into the growing diamond; (iii) *epigenetic*: when they are secondary minerals forming into a pre-existing diamond.

Determining whether an inclusion is syngenetic or protogenetic is of paramount importance in diamond studies. Indeed, any geological information concerning a syngenetic inclusion (i.e., pressure and temperature of formation, age, geochemistry of the mother-medium) is applicable to the host diamond: accordingly, a wrong interpretation concerning the genesis of the diamond-inclusion couple could address to a misleading idea about the geological processes involved in the diamond formation.

The most common proof invoked to establish if an inclusion is syngenetic lies in the imposition of the morphology of the diamond on the inclusion (e.g., Sobolev, 1977; Harris, 1968a). Such a traditional criterion is based on the belief that diamond can impose its cube-octahedral morphology upon the inclusion only during their mutual growth. However, this is not supported by

any chemical-physical arguments, and even less by experimental evidences. Recently, the morphologic criterion has been strongly criticized (Bruno et al., 2014; Nestola et al., 2014; Taylor and Anand, 2004; Taylor et al., 2003). In particular, by analysing the diamond-imposed morphology (Bruno et al., 2014) and the orientations (Nestola et al. 2014) of 43 olivine inclusions in 20 diamonds from the world-famous Udachnaya kimberlite in Siberia (Russia), the authors found that many, if not most, olivine inclusions in diamonds are protogenetic and the diamond-imposed morphology alone cannot be considered as a compelling proof of syngenesis of mineral inclusions in diamonds.

The identification of an epitaxy, on the base of the orientation of the inclusion with respect to its host (Pearson and Shirey, 1999; Harris and Gurney, 1979; Orlov, 1977; Sobolev, 1977), has been considered as a further proof of syngenesis. Unfortunately, the only two works reporting a statistically significant collection of data, have been recently published by Nestola et al. (2014) on the Udachnaya diamonds and Neuser et al. (2015) on the Yubileinaya diamonds (Yakutia). In both papers, the olivine inclusions were shown to be randomly oriented with respect to the hosting diamond: Nestola et al. (2014) performed X-ray diffraction measurements, whereas Neuser et al. (2015) carried out an EBSD analysis in order to determine the crystallographic orientations of the inclusions. Previous works only reported limited sets of samples that are not sufficient to identify, on a firm statistical ground, the mutual orientations between the crystallographic axes of the inclusion and those of the host diamond (Frank-Kamenetsky, 1964; Futergendler and Frank-Kamenetsky, 1961; Mitchell and Giardini, 1953). Moreover, the majority of these papers did not consider the crystallographic contact planes (CCPs) defining the epitaxial interface. The latter information is necessary to asses unambiguously a *preferential* epitaxial relationship since, on a purely geometrical point of view, no constraints can be required on the contact plane of two different phases with the same crystallographic orientation, the number of CCPs being potentially infinite (Fig. S1, Supplementary Material). Indeed, if the inclusions do not show a systematic preferential orientation with respect to diamond (random orientations), one is allowed to state that

there cannot be preferential epitaxial relationships, yet undefined. Conversely, the absence of preferential orientation relationships is not sufficient to conclude that there is not an epitaxial growth, as we will show in this work. Accordingly, it is evident that the *epitaxial criterion* to define syngenesis can result rather ambiguous, if no information can be found on the thermodynamic properties of the epitaxial interface.

Here, we focus on the study of the epitaxial phenomena in olivine-diamond system by an *ab initio* quantum-mechanical computational approach, as such crystal features cannot be experimentally investigated. Olivine forms a complete isomorphous series, with composition ranging from forsterite (Mg_2SiO_4, Fo) to fayalite (Fe_2SiO_4, Fa). However, typical Earth's mantle olivines are Mg-richer ($Fo_{92}Fa_8$) (e.g., Nestola et al., 2011). For this and for sake of simplicity, the fayalite contribution in our model system was neglected. We investigated the $(001)_D/(001)_{Fo}$, $(001)_D/(021)_{Fo}$, and $(111)_D/(001)_{Fo}$ epitaxial interfaces determining their structures and thermodynamic properties. In detail, the specific adhesion energy $\beta^{D/Fo}_{(hkl)/(h'k'l')}$ (i.e., the energy gained, per unit area, once the interface is formed) and the specific interface energy $\gamma^{D/Fo}_{(hkl)/(h'k'l')}$ (i.e., the energy needed to create, per unit area, the interface), were calculated; (*hkl*) and (*h'k'l'*) define the crystallographic faces in epitaxy of D and Fo, respectively. We decided to study the $(001)_D/(001)_{Fo}$, $(001)_D/(021)_{Fo}$ and $(111)_D/(001)_{Fo}$ interfaces for two reasons: (i) the $(001)_D$, $(111)_D$, $(001)_{Fo}$ and $(021)_{Fo}$ are important faces in the crystal morphology of diamond and olivine (e.g., Bruno et al., 2014; De La Pierre et al., 2014); (ii) from a computational point of view, these systems are workable with the resources of calculus actually in our hand.

2. Calculation

The calculations were performed with the *ab initio* CRYSTAL09 code (Dovesi et al., 2009; Dovesi et al., 2005; Pisani et al., 1988) and at the DFT (Density Functional Theory) level with the B3LYP Hamiltonian (Stephens et al., 1994; Becke, 1993; Lee et al., 1988), which provided accurate results for the surface properties of the minerals considered in the present work (Bruno et al., 2014; De La

Pierre et al., 2014; Demichelis et al., 2015). Further computational details (e.g., basis set, thresholds controlling the accuracy of the calculations) are given as Supplementary Material.

A composed slab (D/Fo/D), made by diamond (D) and forsterite (Fo) (slab D and slab Fo hereinafter), was generated in the following way: (i) the two-dimensional (2D) coincidence lattices between the two phases in epitaxial relationship were identified (Bruno et al. 2015); (ii) the slabs D and Fo of a selected thickness were made by cutting their respective bulk structures parallel to the *hkl* planes of interest and using the same 2D cell parameters describing the epitaxy; (iii) the slab Fo was placed in between two slabs D; (iv) finally, the composed slab structure (atomic coordinates and 2D cell parameters) was optimized by considering all the atoms free to move. The slab D/Fo/D was generated preserving the symmetry centre, to ensure the vanishing of the dipole component perpendicular to the slab. The CRYSTAL09 output files, listing the optimized fractional coordinates and optimized 2D cell parameters of the composed slabs, are freely available at http://mabruno.weebly.com/download. The calculations were performed by considering composed slabs with a thickness sufficient to obtain an accurate description of the interfaces. The slab thickness is considered appropriate when the bulk-like properties are reproduced at the centre of the slabs D and Fo. Further details are given as Supplementary Material.

The specific adhesion energy, $\beta^{D/Fo}_{(hkl)/(h'k'l')}$ (J/m^2), is calculated by means of the relation:

$$\beta^{D/Fo}_{(hkl)/(h'k'l')} = \frac{E(2D) + E(Fo) - E(2D + Fo)}{2S} \quad (1)$$

where E(2D+Fo), E(2D) and E(Fo) are the static energies at 0K of the optimized slab D/Fo/D, slab D/vacuum/D and slab Fo, respectively, and S is the area of the surface unit cell. Accordingly, the surface energy is calculated:

$$\gamma^{i}_{(hkl)} = \frac{E(i) - E_b(i)}{2S}; \; i = \text{D, Fo} \quad (2)$$

where $E_b(i)$ is the bulk energy of the *i*-th phase and the factor of 2 in the denominator accounts for the upper and lower surfaces of the slab model.

3. Results and discussion

In Fig.1, the optimized structure of the $(001)_D/(001)_{Fo}$ interface is reported; the $(111)_D/(001)_{Fo}$ and $(001)_D/(021)_{Fo}$ interfaces are given in Figs. S2 and S3 (Supplementary Material). A detailed structural analysis of the interfaces is out of the scope of this work, therefore only a qualitative and short description is given in the following. People interested to an in-depth structural analysis can carry out it by using the CRYSTAL09 output file reporting the optimized atomic coordinates.

The significant structural modifications we observe at the three interfaces are not due to a strong *chemical* interaction between the two phases, as it ensues from the comparison of the relaxed structures of the surfaces in contact both with vacuum and the other mineral (Fig. 1 and Figs. S2-S4). Indeed, the relaxation of the $(001)_D$ and $(111)_D$ surfaces in vacuum (De La Pierre et al., 2014) only slightly differs from that observed when they are in contact with the (001) and (021) faces of forsterite. To describe this geometry modification, we define the roughness of the carbon layer at the interface with the parameter Δz (i.e., the difference between the z coordinates of the carbon atoms within the same layer). Δz is 0.0206 Å for the carbon layer of the $(001)_D$ surface in vacuum, whereas Δz is 0.2144 Å and 0.1712 Å for the carbon layer in contact with $(001)_{Fo}$ and $(021)_{Fo}$, respectively. An analogous relaxation was reported by Bruno et al. (2015) for the $(110)_D$ surface: Δz = 0.0038 Å for the carbon layer in vacuum and Δz = 0.1966 Å for the one in contact with $(101)_{Fo}$. For the $(111)_D$ surface, the relaxation is smaller: Δz = 0.0028 and Δz = 0.0298 Å for that in vacuum and in contact with $(001)_{Fo}$, respectively.

Similarly, the $(001)_{Fo}$ and $(021)_{Fo}$ surfaces are slightly affected by the presence of the diamond. The strong distortion of the SiO_4 tetrahedra in proximity of the outmost diamond surfaces is analogue to that found for the surface in vacuum. Majors differences are due to the distortion and rotation of

some SiO_4 tetrahedra to form C−O bonds in the $(001)_D/(001)_{Fo}$ and $(110)_D/(101)_{Fo}$ (Bruno et al., 2015) interfaces.

Table 1. Optimized 2D cell parameters, adhesion and interfacial energies for the diamond/forsterite epitaxies. The interfacial energies are calculated through Dupré's relation (e.g., Mutaftschiev, 2001) and the following surface energy values: $\gamma^{D}_{(001)}$ = 4.820, $\gamma^{D}_{(111)}$ = 3.849, $\gamma^{D}_{(110)}$ = 5.046, $\gamma^{Fo}_{(001)}$ = 1.676, $\gamma^{Fo}_{(021)}$ = 1.900 and $\gamma^{Fo}_{(101)}$ = 1.696 J/m^2. The data for the $(110)_D/(101)_{Fo}$ interface are from Bruno et al. (2015).

interface	atoms	a (Å)	b (Å)	a^b (°)	area (Å^2)	β (J/m^2)	γ (J/m^2)
$(001)_D/(001)_{Fo}$	184	10.2382	4.9614	89.67	50.80	0.391	6.105
$(111)_D/(001)_{Fo}$	184	4.9899	9.9466	119.79	43.07	-0.934	6.459
$(001)_D/(021)_{Fo}$	304	4.9486	15.4411	89.95	76.41	0.243	6.477
$(110)_D/(101)_{Fo}$	280	7.4210	10.0444	90.09	74.54	0.367	6.375

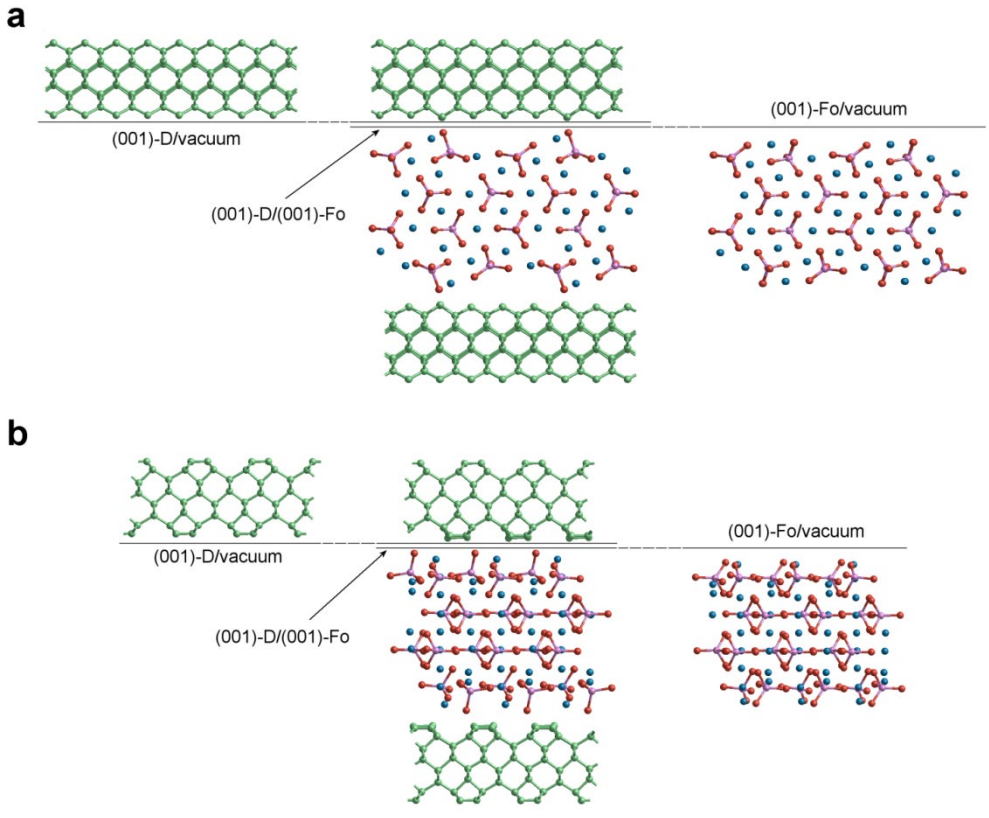

Fig. 1. Optimized $(001)_D/(001)_{Fo}$ (middle), $(001)_D$/vacuum (left) and $(001)_{Fo}$/vacuum interfaces (right). The slabs are viewed along the (a) [110] and (b) $[1\,\bar{1}\,0]$ directions of diamond. Mg, Si, O, and C are blue, pink, red, and green, respectively. The black lines are a guide for eyes to indicate the interfaces.

The weak interaction localized at the D/Fo interface can be ascribed to the extreme rigidity of the diamond surfaces and to the noteworthy difference between the crystal fields belonging to the two phases. Such structural incompatibility generates very low and similar values of the adhesion energy (Table 1) for the $(001)_D/(001)_{Fo}$, $(001)_D/(021)_{Fo}$ and $(110)_D/(101)_{Fo}$ (Bruno et al., 2015) interfaces, 0.243-0.391 J/m^2 (differences are within the calculation accuracy), and even a negative one for the $(111)_D/(001)_{Fo}$ interface, -0.934 J/m^2. Interestingly, different values of $\beta^{D/Fo}_{(hkl)/(h'k'l')}$ provide very similar values of $\gamma^{D/Fo}_{(hkl)/(h'k'l')}$ (Table 1) when the Dupré's relation (e.g., Mutaftschiev, 2001) is used ($\gamma^{D/Fo}_{(hkl)/(h'k'l')} = \gamma^{D}_{(hkl)} + \gamma^{Fo}_{(h'k'l')} - \beta^{D/Fo}_{(hkl)/(h'k'l')}$), where $\gamma^{D}_{(hkl)}$ and $\gamma^{Fo}_{(h'k'l')}$ are the surface energies in the vacuum of diamond and forsterite): 6.105-6.477 J/m^2. The implications of these findings are numerous and outstanding. The epitaxy between the (111) face of diamond and forsterite results to be very likely impossible. However, further calculations on epitaxial systems involving the $(111)_D$ and other forsterite surfaces could be performed to verify this statement. The (110) and (001) faces of diamond show an undifferentiated behaviour with regard to forsterite; they seem to have the same probability to make epitaxy with whatever surface of forsterite. According to the classical nucleation theory (e.g., Mutaftschiev, 2001), lower the adhesion energy, lower the probability of the 3D-heterogeneous nucleation to occur (i.e., the formation of 3D nuclei of a phase A above a phase B), the 3D-homogeneous nucleation becoming competitive as much as $\beta^{D/Fo}_{(hkl)/(h'k'l')}$ approaches to zero. When $\beta^{D/Fo}_{(hkl)/(h'k'l')}$ is negative, as for the $(111)_D/(001)_{Fo}$ interface, a very peculiar case is spotted: the homogeneous nucleation could occur more likely than the heterogeneous one.

An extremely interesting consequence of our calculations concerns the impossibility of the diamond-forsterite system to develop a preferential orientation during any possible epitaxial growth. This is in agreement with the recent crystallographic observations reported by Nestola et al. (2014) and Neuser et al. (2015), where no overall preferred orientation of olivines in diamond was found. It is evident that our results cast serious doubts on the application of the mere crystallographic

196 measurements of the relative orientations of diamond and olivine inclusions to hypothesize epitaxy
197 and, eventually, syngenesis. Indeed, if a preferential crystallographic orientation between inclusion
198 and host is not observed, this does not mean that the epitaxy cannot be realized; on the contrary,
199 epitaxy could occur through several D/Fo interfaces owing to the quasi-invariance of their adhesion
200 energy. Other silicate inclusions in diamond, with their outmost surfaces exhibiting SiO_4 tetrahedra,
201 like olivine, could show analogous behaviour. Preliminary measurements on orientation of garnet
202 inclusion in diamond (F. Nestola, personal communication), where a random distribution is
203 observed, seem to confirm such assumption.

204 Finally, from our findings on the quasi-invariance of the adhesion energies, the *epitaxial*
205 *criterion* alone results to be not adequate to discriminate between syngenesis and protogenesis in
206 the case of diamond-olivine pair. Three scenarios can be depicted to explain this concept. First, we
207 suppose a protogenetic origin for olivine: diamonds form from a carbon-rich fluid or melt
208 percolating homogeneously through an olivine-rich mantle rock (i.e., peridotite), by nucleating and
209 growing indifferently onto any olivine surfaces. Then, diamonds continue growing and fragments of
210 pre-existing olivine are entrapped. This represents a highly favorable scenario, since the mantle
211 rock is mainly composed by olivine and heterogeneous nucleation is always favored with respect to
212 the homogeneous one when $\beta^{D/Fo}_{(hkl)/(h'k'l')}$ is positive. Such a path should generate a rock containing
213 randomly oriented diamonds.
214 The second scenario accounts for a syngenetic origin of olivine inclusions: diamond nucleates
215 somewhere within the rock and, at a certain point of its history, olivines nucleate and grow on
216 diamond surfaces during its ongoing growth, without developing a preferential epitaxial
217 relationship, due to the quasi-invariance of $\beta^{D/Fo}_{(hkl)/(h'k'l')}$ values. Then, as for the protogenetic case, the
218 new formed olivines are entrapped in the growing diamonds without any preferential orientation.
219 In the last scenario, diamonds and olivines form through a homogeneous nucleation in the fluid.
220 Without an epitaxial control, no preferential crystallographic orientation can be developed: also in
221 this case, a rock having diamonds and its olivine inclusions with random orientations should be

obtained.

Summing up, no overall preferred orientation of olivines in diamond can be identified in a mantle rock, both for syngenesis and protogenesis, as well as both in the case of heterogeneous and homogeneous nucleation. Combining our results with those of Bruno et al. (2014) concerning the morphology imposition by diamond on its inclusions, we can state that the two main arguments playing in favour of syngenesis between diamond and its inclusions cannot be longer considered valid. Alternative explanations must be provided to demonstrate the growth relationship between diamond and its inclusions.

4. Conclusions

In this work, both the structure and energetics of the $(001)_D/(001)_{Fo}$, $(001)_D/(021)_{Fo}$, and $(111)_D/(001)_{Fo}$ epitaxial interfaces were determined for the first time by means of *ab initio* quantum-mechanical simulations. Our results can be summarized as follow:

(i) Diamond and forsterite have an extremely low chemical affinity: all interfaces show almost equal and low adhesion energies.

(ii) From our findings on the quasi-invariance of the adhesion energies we can state that the diamond-forsterite system is not able to develop a preferential orientation during any possible epitaxial growth. Then, no overall preferred orientation of olivines in diamond can be identified in a mantle rock.

(iii) The two main arguments in favour of syngenesis (i.e., morphologic and epitaxial criteria) between diamond and its inclusions are not valid, at least for olivine. Alternative explanations must be provided to demonstrate the growth relationship between diamond and its inclusions.

(iv) Other silicate inclusions (e.g., coesite, garnet, pyroxene) in diamond could show an analogous behaviour to that of the olivine.

(v) It is important to highlight that we determined the adhesion energies by performing the calculations at $T = 0$K and $P = 0$. To take into accounts the effect of T and P on the adhesion energy

very demanding calculations should be done, which cannot be actually performed with the computational resources at our disposal. Moreover, at the best of our knowledge, there are not works in which the effect of *T* and *P* on the energetics of the epitaxial interfaces is discussed. This lack of information prevents to know the behaviour of the adhesion energies when both temperature and pressure increase. To have a realistic estimate of the effect of temperature for the different diamond/forsterite interfaces, it is necessary to determine at *ab initio* level the frequencies of the vibrational modes of the composed slabs, which are essential for calculating the vibrational contribution (i.e., vibrational energy and vibrational entropy) to the interface energy of an epitaxial system (e.g., Bruno, 2015; Bruno and Prencipe, 2013).

(vi) We performed the simulations by considering an olivine formed exclusively by the forsterite end-member (Fo_{100}). Nevertheless, typical Earth's mantle olivines contain a small percentage of iron (~$Fo_{92}Fa_{8}$), which could affect the values of the adhesion energies. Even in this case there are not estimates of the effect of iron on the interaction between diamond and olivine. There is only a very recent work (Navarro-Ruiz et al., 2014) where the authors calculated at *ab initio* level the surface energy (at 0K and in the vacuum) of the (010) face of Mg-pure (Fo_{100}) and Fe-containing ($Fo_{75}Fa_{25}$) olivines. The authors found that the (010) surface energy for $Fo_{75}Fa_{25}$ (0.870 J/m^2) is lower by 25% than the (010) surface energy for Fo_{100} (1.160 J/m^2). This means that the iron has certainly a strong effect on the values of the surface energy of the olivine faces and that it is licit to expect that also the adhesion energies could be affected by the presence of fayalite. Hovewer, since the mantle olivines are poor in fayalite, it is likely that our estimates of adhesion energy values are only slightly modified by the content of iron. Unless this latter tends to segregate preferentially onto the crystal surfaces of olivine, by increasing the fayalite content at the diamond/olivine interface. Such phenomenon was observed for Ca^{+2} in magnesium silicate olivine rich aggregates by Hiraga et al. (2004) and energetically analysed by Alfredsson et al. (2005) for an orthorhombic $MgSiO_3$-perovskite.

(vii) Another point to address is the following. We cannot state with absolute certainty that diamond

and olivine are in direct contact between them. It should be possible that a very thin layer (a few Ångström thick?) of a fluid (or 2D solid) phase takes place in between diamond and olivine, so forming a more complex interface. Obviously, only the experimental observation on natural samples can give a definitive answer to such a question. It is sure yet that if a similar complex interface exists, then the adhesion energies between diamond and olivine are completely different from those determined in this work. It is for posterity to judge…

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