Frenkel pair formation energy for cubic Fe$_3$O$_4$ in DFT + U calculations

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Abstract
The cubic phase of magnetite is stabilized above the Verwey transition temperature of about 120 K via a complex electron–phonon interaction that is still not very well understood. In this work using the DFT + U method we describe our attempt to calculate point defect formation energies for this cubic phase in the static approximation. The electronic structure calculations and atomic relaxation peculiarities are discussed in this context. Only the cubic phase model with a small band gap and charge disproportionation (Fe$^{2+}$/Fe$^{3+}$) gives an adequate point defect formation energies, not the semi-metallic model. The relaxation of the local defect atomic structure and the relaxation of the surrounding crystal matrix are analyzed. Point defects cause only local perturbations of atomic positions and charge-orbital order. After analysis of the supercell size effects for up to 448 atoms, we justify the use of small supercells with 56 atoms to make calculations for the cubic phase. The extensive experimental results of Dieckmann et al on defects in magnetite at high temperature are deployed for comparison of our DFT + U results on Frenkel pair formation energies.

Keywords: magnetite, ab initio, point defects, vacancy, interstitial

(Some figures may appear in colour only in the online journal)

1. Introduction

Being among the oldest materials known to the mankind, magnetite is still not well understood in the framework of the solid state theory. Magnetite exhibits ferrimagnetic ordering below 858 K and becomes paramagnetic at higher temperatures. At the Verwey transition temperature $T_V \sim 125$ K magnetite shows a sudden rise in conductivity and transforms from the low temperature monoclinic phase into the high temperature inverse spinel (cubic) phase [1]. The puzzle of the Verwey transition is an important topic in the physics of strongly correlated systems that attracts a lot of attention [2] and ignites controversies [3].

The Verwey transition studies require in-depth analysis of both the monoclinic low temperature phase and the cubic phase that becomes stable above $T_V$. A new type of local structures called trimeron were identified in the low temperature phase [4]. Trimeron can be described as highly structured three-site polarons and can be considered as an example of orbital molecules or clusters made up of coupled orbital states on several metal ions within an orbitally ordered solid [5]. There are strong experimental evidences that the trimeron order exists at temperatures above $T_V$ [6]. In another experiment, however, trimeron correlations in the cubic phase have not been detected [7].
Under normal conditions at $T > T_1$, magnetite has an inverted spinel structure with the space group Fd3m (figure 1). The formula Fe$_3$O$_4$ can be also written as Fe$^{3+}$(Fe$^{2+}$Fe$^{3+}$)$_2$O$_4$~. The letters A- and B- denote the tetrahedral and octahedral sites in cubic magnetite and also its magnetic sublattices. In such a structure, different types of cation point defects can be distinguished: vacancies in both cation sublattices (A- and B-), as well as interstitial atoms of at least three types (figure 1). In addition, the formation of oxygen defects is unlikely but can not be excluded at all. Such a variety of defect structures makes the interpretation of experimental data on point defects in magnetite an unsolvable problem without a priori assumptions about predominant defect types.

The recent core-level x-ray spectroscopy measurements have given new information on the cation ordering at temperatures up to 1200 K [9] including the formation of cation Frenkel pairs (FPs). This experiment sheds new light on the previous thorough studies of high temperature properties of magnetite by Dieckmann et al [10–17] and emphasizes the role of point defects in understanding the properties of magnetite at high temperatures. Dieckmann et al showed that at low oxygen activity (i.e. low oxygen chemical potential) cation interstitials are responsible for the cation diffusion, while at high oxygen activity vacancies in the cation sublattice are predominant. One of the results of the extensive experimental studies of Dieckmann et al is the value of the cation FP formation energy in magnetite $E_\text{FP}^{\text{c}} = 1.38$ eV at about 1200 K [15]. The FP formation energy $E_\text{FP}$ is a better defined property than the formation energies of vacancies and interstitial atoms since $E_\text{FP}$ does not depend on oxygen activity. We are not aware of any published attempts to calculate $E_\text{FP}$ in cubic magnetite and to make a comparison with the result of Dieckmann et al. At the same time, calculations of the FP formation energy by ab initio methods could serve as a valuable benchmark of the theoretical approaches available for description of magnetite.

First principles modeling of magnetite has a long history (e.g. see [18–46]). However, only several studies were devoted to point defect properties [21, 36, 38, 40, 42, 46]. The formation energies of cation defects have been obtained by Hendy et al within the pure DFT framework [21]. According to [21], the defect with the lowest formation energy in magnetite is the vacancy of B-sublattice and $E_\text{FP}^B = 4.09$ eV. Hendy et al [21] have made an attempt to describe the electronic properties of defect configurations, but this description remains unclear without special consideration for strong electronic correlations. Such a description within the DFT + U framework has been obtained later by Arras et al [38]. However, nothing was said in [38] about the formation energies of the defects considered. Earlier, Arras et al considered the effect of oxygen vacancies on electronic structure of cubic magnetite [36]. We are aware of the only work of Li et al [40] where the formation energies of defects in magnetite were calculated within DFT + U. However, there are very significant differences between the data obtained in DFT [21] and DFT + U [40] on the defect formation energies. The calculation procedure of Li et al [40] suggests that their formation energies correspond better not to the cubic phase but to the low temperature phase of magnetite (their approach gives $E_\text{FP}^c = 3.11$ eV). Using DFT + U, Muhich et al calculated the energy of vacancy migration between octahedral positions and the vacancy formation energy difference for tetrahedral and octahedral positions [41]. In our recent paper [46], we have analyzed the DFT + U approximations for magnetite.
cubic phase and have presented the results of vacancy formation energy calculations without any comparison with experiments.

This paper has the following structure. In section 2 we describe the details of the model and the calculation method. In section 3 the results are presented for the cubic and low-T reference defect-free structures, for cation interstitials, vacancies and FPs, and for the influence of the system size and the Hubbard U parameter. In section 4 we discuss the results and make comparisons with experimental data available.

2. Model and calculation details

All calculations in this work are performed within the density functional theory (DFT). Strong electronic correlations are taken into account by the DFT + U approach [47–49] using the Dudarev’s scheme [50] with $U_{\text{eff}} = U - J$. The main part of calculations are performed using $U_{\text{eff}} = 3.5$ eV. The influence of $U_{\text{eff}}$ on the results is considered as well (see section 4).

Only collinear magnetism is considered in the work.

The calculations are carried out with the VASP package [51–53]. The main results for the cubic phase point defects are obtained in a cubic supercell with 56 atoms (the conventional cell of cubic magnetite). The size effects are also investigated in supercells with up to 448 atoms (i.e. the 56 atom supercell replicated $2 \times 2 \times 2$). For summation over the Brillouin zone, $6 \times 6 \times 6$ and $3 \times 3 \times 3$ $\Gamma$-centered k-point meshes are used in supercells with 56 and 448 atoms, respectively. The plane wave basis cutoff energy is set to 550 eV in all cases. The generalized gradient approximation with the Perdew–Burke–Ernzerhof parametrisation (GGA PBE) [54] is used for the exchange-correlation functional. The total energy convergence threshold is $10^{-6}$ eV. Due to the local minima problem inherent to DFT + U, a resulting self-consistent solution at fixed ionic positions strongly depends on the initial guess for electron density.

Configurations of the cubic Fd3m phase are obtained at the experimental value of the magnetite oxygen coordinate $x = 0.2549$ [55]. The optimized cubic phase lattice constant $a_0$ corresponds to the zero trace of the external stress tensor ($a_0$ is optimized at the fixed $x$).

We consider two types of defect-free configurations of the cubic Fd3m phase: the configurations with all cations fixed at their high symmetry position and the configurations with internal parameters allowed to relax via geometry optimization at the fixed supercell shape. The former case is considered as a model of cubic temperature-stabilized magnetite above $T_V$. The latter case is considered as an approximate model of the low-temperature phase below $T_V$ (according to the experiments the low-T phase is monoclinic [4] but it was shown that the cell shape relaxation has a minor contribution for energy minimization [44]). Different types of relaxation of atomic positions in calculations of point defects are considered: either starting from a cubic structure, or starting from a relaxed structure. The geometry optimization convergence threshold is $10^{-2}$ eV Å$^{-1}$ (determined from the forces acting on atoms). A resulting atomic structure after atomic relaxation depends on the initial structure and on the initial guess for electron density [56].

The formation energy of an isolated defect $E_{\text{def}}^{f}$ is calculated using [57]:

$$E_{\text{def}}^{f} = E_{\text{def}} - E_0 \pm E_{\text{at}},$$

where $E_{\text{def}}$ and $E_0$ are the total energies of the supercell with and without a defect (a vacancy $E_V$ or an interstitial $E_I$). Here, $E_{\text{at}}$ is the chemical potential of the removed (or added) atom. $E_{\text{at}}$ is chosen as the energy per atom in ferromagnetic body-centered cubic iron for the same $U_{\text{eff}}$. The choice of $E_0$ plays an important role in this work since we can take $E_0$ either for the ideal cubic phase or for the relaxed low-T phase with atomic distortions. This choice is crucial for the resulting values of $E_{\text{def}}^{f}$ and for their interpretation.

The formation energy of a FP $E_{\text{FP}}^{f}$ is calculated as

$$E_{\text{FP}}^{f} = E_V + E_I - 2E_0,$$

where $E_V$ and $E_I$ are the total energies of the supercells with a vacancy and with an interstitial.

A defect is created in the defect-free cubic phase configuration. Atomic relaxation is performed at the fixed optimized lattice constant. There are two types of cation vacancies in the cubic phase of magnetite: the vacancies in A- and B-sublattices (figure 1). Previously, we have shown that the vacancy of the B-sublattice has the lowest formation energy [46]. Three types of initial sites for interstitial defects are considered (figure 1).

In the A1-int case, the defective cation is located inside the tetrahedron of B-cations. In the A2-int case, two B-cations and two A-cations are the closest atoms to the interstitial atom. The B-int case, the octahedral interstitial cation occupies the octahedral interstitial site that is free in the defect-free crystal.

3. Results

3.1. Defect-free cubic phase

In our previous work, the solution $m2$ (denoted as -545(m2) in [46]) was found to have one of the lowest total energies for the defect-free magnetite cubic phase. This solution was obtained without imposing any additional symmetry constraints on Kohn–Sham orbitals and on electron density. The main features of $m2$ that has the Verwey-type charge-orbital ordering are presented in figure 2.

A solution calculated using additional symmetry constraints (according to the cubic lattice symmetry) on Kohn–Sham orbitals and electron density is obtained in this work for comparison. This solution is denoted as $\text{sym}$. The total energy of this symmetric solution turned out to be higher than the total energy of the asymmetric solution $m2$ by 0.287 eV/f.u.

Properties of the symmetric solution are shown in figure 3. In contrast to the $m2$ case, there are no differences between di- and trivalent cations in the symmetric case [43]: all the
Figure 2. Properties of the asymmetric solution $m^2$: the magnetic moments of the A- and B-cations ($N = 1 \div 8$ and $N = 9 \div 24$, respectively), the total and projected onto atomic groups densities of states (the black curve and the curves of different colors), the spatial distribution of the electron density related to the peak located just below the Fermi level ($t_{2g}$ orbitals of Fe$^{2+}$ cations). The Fermi level is shown as a gray dotted vertical line. The densities of spin-up and spin-down states are plotted up and down the $y$-axis.

B-cations have the same magnetic moment (figure 3, top picture). Also, one can see no differences between Fe$^{2+}$ and Fe$^{3+}$ B-cations in the spatial distribution of the partial electron density, plotted for the bands just below the Fermi level (figure 3, bottom picture). In the symmetric case, there is no gap in the electronic density of states (DOS) at the Fermi level.

The asymmetric and symmetric solutions give different values of the lattice constant at zero trace of the stress tensor for the cubic phase: 8.456 Å and 8.479 Å for $m^2$ and $sym$, respectively, at fixed $x = 0.2549$. At this lattice constant not only the trace of the stress tensor, but also all its components are equal to zero in the symmetric case. In the asymmetric case, on the contrary, the stress tensor components are nonzero and, in addition, nonzero forces act on atoms (up to 0.4 eV Å$^{-1}$ and 0.75 eV Å$^{-1}$ on cations and anions, respectively). Therefore, as soon as ions are allowed to change positions in the asymmetric case the ideal cubic lattice becomes distorted.

3.2. Atomic relaxation in the defect-free case

The optimization of atomic coordinates in the defect-free case is performed with and without additional symmetrization of the electron density. No change occurs in the former case. In the latter case the cubic structure becomes distorted significantly [46]. The ferrimagnetic ordering, the total magnetic moment, and the distribution of the di- and trivalent cations over B-sites do not change after the relaxation. The largest change in the magnetic moments of cations does not exceed 0.02 $\mu_B$. The main changes after relaxation are [46]: (1) the slight rotations of the orbitals and (2) the distortions of the cubic structure.

In this work, the attention is paid to the geometry of the structure after atomic relaxation in the defect-free case (figure 4). The distortions of octahedra and tetrahedra are
clearly visible after relaxation. Indeed, all of the tetrahedra are equal in the undistorted cubic phase. The same can be said about all octahedra. After relaxation the situation changes. There are two types of octahedra in the relaxed structure, with larger and smaller volume, corresponding to di- and trivalent cations, respectively. Fe$_A$–O distances in tetrahedra are not equal, the same can be said about Fe$_B$–O distances in octahedra. Fe$_B$–Fe$_B$ distances change as well (see section 4).

3.3. Cation interstitials

Three initial positions of interstitial atoms A1, A2 and B (see figure 1) are considered in the supercell with 56 atoms. Five different initial approximations to the initial magnetic moment of the defective cation (0, ±4, ±5) are investigated. The properties of the optimized structures are presented in table 1. In contrast to pure DFT, the DFT + U point defect model is sensitive not only to the direction, but also to the magnitude of the initial magnetic moment.

After the geometry optimization, the defective cation is displaced from its initial site by a distance $\Delta r$. This distance in some cases for the A1- and A2-initial sites is greater than the Fe$_A$–O bond length in the defect-free case, so the interstitial cation leaves the initial interstitial site in these cases. Figure 5 shows the initial and optimized geometries for the defect configurations with the lowest formation energies for the A1- and A2-initial sites. As one can see, some of the nearest cations to the defective atom are also shifted from their initial positions. The coordination change for one of the octahedral cations is observed. The distances between the defective cation and its nearest neighbor cations turn out to be less than the shortest Fe$_B$–Fe$_B$ distance in a defect-free structure.

Our DFT + U results (see table 1) indicate that the interstitial with the lowest formation energy is in the octahedral position (B-interstitial). Pure DFT shows the same in our work (as in [21]). Below, we consider this structure in more details.

3.4. Octahedral interstitial

After the geometry optimization, the octahedral interstitial cation does not leave its initial site ($\Delta r \approx 0$ in table 1) and does not form complexes with other cations. The two nearest to the defective cation A-cations only move away from it slightly. Several solutions with close formation energies 0.32±0.34 eV have been found for the B-interstitial atom. They do not differ significantly from each other (the case $E_{f-B-int} = 0.34$ eV is shown on figures 6 and 7).

Due to the defect formation, the total magnetic moment of the supercell decreases by 6 $\mu_B$. The changes affect mainly the B-cations: the number of divalent B-cations increases,
Table 1. Properties of the optimized interstitial atom configurations in pure DFT and DFT + U (\(U_{\text{eff}} = 3.5\) eV). \(\mu_{\text{Fe}}^0\) (\(\mu_B\)) is the initial approximation to the magnetic moment of the interstitial cation, \(\Delta E = E_{\text{def}} - \bar{E}_0\) (eV) is the difference between defect and defect-free total energies, \(E_{\text{tot}}^0\) (eV) is the defect formation energy, \(\Delta \mu_{\text{tot}} = \mu_{\text{def}} - \mu_0\) (\(\mu_B\)) is the difference in the total magnetic moment between defect- and defect-free supercells, \(\mu_{\text{Fe}}\) (\(\mu_B\)) is the final magnetic moment of the interstitial cation, \(\Delta \rho = \rho_{\text{def}} - \rho_0\) (kbar) is the difference in the external pressure between the defect and defect-free supercells, \(\Delta \varepsilon\) (Å) is the displacement of the interstitial atom from its initial position (A1, A2 or B) after the geometry optimization.

| Defect  | \(\mu_{\text{Fe}}^0\) | \(\Delta E\) | \(E_{\text{tot}}^0\) | \(\Delta \mu_{\text{tot}}\) | \(\mu_{\text{Fe}}\) | \(\Delta \rho\) | \(\Delta \varepsilon\) |
|---------|-----------------------|-------------|-----------------|-----------------|-----------------|-------------|-----------------|
| A-int   | -5.0                  | -2.724      | 2.85            | +2.0            | +3.40 \(\uparrow\uparrow\) Fe\(_B\) | +75.4       | 0.71            |
|         | -4.0                  | -4.674      | 0.90            | +2.0            | +3.42 \(\uparrow\uparrow\) Fe\(_B\) | +52.3       | 2.29            |
| A1-int  | 0.0                   | -4.628      | 0.94            | +2.0            | +3.79 \(\uparrow\uparrow\) Fe\(_B\) | +61.2       | 2.15            |
|         | +4.0                  | -2.765      | 2.81            | +2.0            | +3.40 \(\uparrow\uparrow\) Fe\(_B\) | +75.0       | 0.72            |
|         | +5.0                  | -3.473      | 2.10            | -4.0            | +3.47 \(\uparrow\uparrow\) Fe\(_B\) | +48.3       | 2.23            |
| A2-int  | 0.0                   | -4.802      | 0.77            | +2.0            | +3.41 \(\uparrow\uparrow\) Fe\(_B\) | +52.9       | 0.46            |
|         | +4.0                  | -1.875      | 3.70            | -6.0            | +3.38 \(\uparrow\uparrow\) Fe\(_B\) | +37.2       | 0.18            |
|         | +5.0                  | -2.045      | 3.52            | -8.0            | +3.42 \(\uparrow\uparrow\) Fe\(_B\) | +41.1       | 0.43            |
|         | -5.0                  | -4.550      | 1.02            | +2.0            | +3.61 \(\uparrow\uparrow\) Fe\(_B\) | +39.1       | 0.02            |
|         | -4.0                  | -5.169      | 0.40            | -6.0            | -3.70 \(\uparrow\uparrow\) Fe\(_A\) | +39.5       | 0.01            |
| B-int   | 0.0                   | -5.246      | 0.32            | -6.0            | -3.73 \(\uparrow\uparrow\) Fe\(_A\) | +41.4       | 0.01            |
|         | +4.0                  | -5.238      | 0.33            | -6.0            | -3.71 \(\uparrow\uparrow\) Fe\(_A\) | +40.5       | 0.00            |
|         | +5.0                  | -4.016      | 1.55            | -8.0            | -3.70 \(\uparrow\uparrow\) Fe\(_A\) | +34.4       | 0.01            |
|         | -5.0                  | -5.098      | 3.14\(^a\)      | -6.0            | -3.41 \(\uparrow\uparrow\) Fe\(_A\) | +32.8       | 0.00            |
|         | 0.0                   | -4.302      | 3.94            | -2.0            | +3.28 \(\uparrow\uparrow\) Fe\(_B\) | +16.11      | 0.00            |
|         | +5.0                  | -5.098      | 3.14\(^b\)      | -6.0            | -3.41 \(\uparrow\uparrow\) Fe\(_A\) | +32.8       | 0.00            |
| A-int   | -                     | -           | 5.40            | +2.0            | \(\uparrow\uparrow\) Fe\(_B\)     | -           | -               |
| A-int   | -                     | -           | 1.25            | -               | -               | -           | -               |
| A1-int  | -                     | -           | 1.25            | -               | -               | -           | -               |
| A2-int  | -                     | -           | 1.25            | -               | -               | -           | -               |
| B-int   | -                     | -           | 3.26            | -6.0            | \(\uparrow\uparrow\) Fe\(_A\)     | -           | -               |
|         | -                     | -           | 0.81            | -               | -               | -           | -               |
|         | -                     | -           | -               | -6.0            | \(\uparrow\uparrow\) Fe\(_A\)     | -           | -               |
|         | -                     | -           | -               | -               | \(\uparrow\uparrow\) Fe\(_A\)     | -           | -               |

\(^a\) \(E_{\text{tot}} = 5.57\) eV in DFT + U with \(U_{\text{eff}} = 3.5\) eV.

\(^b\) \(E_{\text{tot}} = 8.24\) eV in pure DFT (\(U_{\text{eff}} = 0\)).

Note: The lowest formation energies for each defect type is shown in bold.

while the number of trivalent B-cations decreases (figure 6). The distribution of di- and trivalent cations over B-sublattice also changes: the divalent cations are located closer to the interstitial, while trivalent cations are located farther (figure 7).

The magnetic moment of the defective cation is co-directional with the magnetic moments of A-cations. The magnitude of the magnetic moment of the defective cation allows it to be classified as a divalent cation. There are no states associated with the defective cation in the valence band (figure 6).

The change in the total magnetic moment of 6 \(\mu_B\) can be explained in a clear way. The magnetic moment of a defect-free supercell is 32 \(\mu_B\) (i.e. 4 \(\mu_B\)/f.u.). The total magnetic moment of the defective configuration equals to 8 \(\cdot\) (−5) \(\mu_B\) + 6 \(\cdot\) 5 \(\mu_B\) + (8 + 2) \(\cdot\) 4 \(\mu_B\) + 1 \(\cdot\) (−4) \(\mu_B\) = 26 \(\mu_B\). Thus, the change in the total magnetic moment is connected, firstly, with the magnetic moment of the defective cation = −4 \(\mu_B\) (as divalent, but \(\uparrow\uparrow\) Fe\(_A\)), and secondly, with the fact that in order to screen this charge, two of the eight trivalent B-cations become divalent.

3.5. Octahedral vacancy

Previously, we have found that the B-vacancy has the lowest formation energy among cation vacancies [46]. This result is consistent with data obtained in other DFT and DFT + U data [21, 38, 40]. However, a new solution for the B-vacancy has been found in this work with the formation energy of 1.20 eV (lower than the previously found minimum by 60 meV). Although other new solutions with even lower total energies could be found, in principle, for vacancies, it would not change their energy hierarchy since the differences in the formation energies of A- and B-vacancies are more than 1 eV.

The properties of the B-vacancy is shown in figures 6 (two bottom pictures) and 7. The ferrimagnetic ordering remains after the defect formation, but the total magnetic moment of the supercell decreases by 2 \(\mu_B\) due to an increase in the number of trivalent cations and a decrease in the number of divalent cations in the B-sublattice (figure 6). In this case, in contrast to the B-interstitial, the trivalent cations become closer to the vacancy (figure 7). The band gap of the defective configuration...
Figure 5. The initial and the optimized geometries of the A1- and A2-initial cites. The cases with the lowest formation energies from table 1 are shown. The defective cation is shown in pink (A1) and green (A2). The polyhedra of the nearest neighbor cations to defective atom are shown.

is larger than the band gap after the atomic relaxation in the defect-free supercell (figure 6).

3.6. Effects of supercell size and $U_{\text{eff}}$

Figure 8 summarizes our data on the defect formation energy dependencies on the number of magnetite formula units ($N_{\text{f.u.}}$) that comprise the supercell. The data for the interstitial and the vacancy with the lowest formation energies and for the corresponding FPs are shown (the details for the smallest and for the largest system sizes are given in table 2). Two variants of formation energies are presented: the variant for cubic phase and the variant for low-$T$ phase (i.e. for two different $E_0$ reference energies). The formation energies for cubic phase are much lower and have a pronounced system size dependence. The formation energies for low-$T$ phase is higher and show quite a moderate variation with the system size. Additionally, the total energy change during the relaxation to low-$T$ phase $E_{\text{rel}}N_{\text{f.u.}}$ is shown on figure 8 by the pink diamonds. The relaxation of the point defect in the cubic phase includes two effects: (a) the distortions that are natural for low-$T$ phase and (b) the distortions that are caused by the point defect itself. As we show below in section 4, this duality explains the pronounced system size effect for cubic phase formation energies and justifies that the $E_{\text{FP}}$ value for the system of 56 atoms should be considered as the best estimate for cubic phase of magnetite.

The $U_{\text{eff}}$ parameter serves as an empirical constant which magnitude governs the Hubbard-like correction to the total DFT energy for strong electron correlations. Figure 9 shows how moderate variations of $U_{\text{eff}}$ influence point defect energies considered. The B-vacancy formation energy grows with $U_{\text{eff}}$ but the B-interstitial formation energy becomes smaller. The combined effect for the FP formation energy results in the decrease of $E_{\text{FP}}$ for larger $U_{\text{eff}}$.

4. Discussion

Stability of the cubic phase of magnetite is a result of the complex mechanism of electron-phonon interaction that is known to have special features in strongly-correlated oxides [58, 59] and is activated in magnetite at above $T_V$. Currently, there is neither a complete theoretical description of this mechanism, nor the possibility to study it numerically using first-principles modeling (e.g. using $ab$ initio molecular dynamics). Presence of local trimeron order above $T_V$ [6] suggests that local instantaneous atomic configurations
Figure 6. The properties of the B-interstitial (two upper pictures) and the B-vacancy (two lower pictures). The designations are as in figure 3. The magnetic moment of the defective cation has the number $N = 0$.

during some fraction of time do not correspond to the cubic phase and possess certain traits of the low temperature phase. That is why making electronic structure calculations for ideal cubic structure of magnetite is a reasonably simplified and computationally feasible approximation for the problem of modeling the cubic phase of magnetite. The methods for proper nonadiabatic dynamics of condensed matter systems are discussed (e.g. see [60–64]) and could be applied to this problem in the future.
Our calculations of the low-T phase include relaxation of atomic positions only. We do not relax the shape of the supercell since it was shown [44] that allowing cell shape to distort to monoclinic resulted in the total energy reduction of 0.008 eV/f.u. only. Another simplification is that we use the supercell with 56 atoms while experimental data suggest that the low-T phase unit cell consists of 224 atoms. The main focus of this work is the cubic phase and the results for the low temperature phase are needed for comparison.

In this work, we consider only one charge-orbital pattern m2 corresponding to the Verwey scheme. Previously [46], we have shown that for the supercell of 56 atoms it is possible to obtain different self-consistent DFT + U local minima for cubic phase with the total energy variation of several meV only. In addition to m2, there is at least one other solution without charge ordering that has been found to provide the same lowest total energy [46]. The similar multitude of ground state structures have been discovered in [28] for the low-T phase. The range of relaxed total energies was ~0.02 eV/f.u. and the structures with the Verwey charge order had energies in the middle of this range [28, 44]. Zhou and Ceder [34] used the cluster expansion approach to parameterize the charge-orbital space of relaxed low-T structures obtained in DFT + U. The existence of the multitude of ground state structures with different charge-orbital patterns and very close total energies (both for the cubic phase and for the low-T phase) justifies our consideration of the m2 charge-orbital pattern only for both the cubic and low-T reference state energies \( E_0 \) that are used in calculations of defect formation energies.

The top left picture in figure 10 shows the m2 structure in the supercell with 56 atoms after atomic relaxation to the low-T phase from the initial ideal cubic structure with the same charge-orbital m2 pattern (figure 2). The details of Jahn–Teller distortions in this structure have been illustrated in figure 4. On figure 10 the triplets of B-cations \((\text{Fe}^{3+}_B - \text{Fe}^{3+}_B - \text{Fe}^{3+}_B)\) are marked by the line segments. In these triplets we observe the same \( \text{Fe}^{3+}_B - \text{Fe}^{3+}_B \) distances of 2.932 Å shortened by 2%
compared to the Fe$_{\text{B}}^{2+}$–Fe$_{\text{B}}^{3+}$ distance of 2.998 Å in the cubic phase. Other Fe$_{\text{B}}^{2+}$–Fe$_{\text{B}}^{3+}$ distances (not shown in figure 10) become longer than in the cubic phase. These triplets form parallel chains and the $t_{2g}$ orbitals are oriented strictly in accordance with these chains. One can see clearly the manifestation of the trimeron order \([4, 5]\). The top right picture in figure 10 shows the result of the atomic relaxation in the similar 55-atom structure with a B-vacancy. No signs of chains of triplets of B-cations remain after relaxation. Three lower pictures in figure 10 show the similar relaxed B-vacancy for the supercell with 111, 223 and 447 atoms. In this case the chains of triplets remain. The presence of a vacancy does not destroy this ordering. This difference between the smaller (55 atoms) and larger B-vacancy models shows explicitly that there are 2 relaxation effects: (a) the relaxation of the cubic phase to the low-$T$ phase and (b) the local relaxation due to the defect formation. The contribution to the total energy change from the first effect is proportional to $N_{\text{vac}}$ (as shown on figure 8). That is why the defect formation energies for the cubic phase have such a strong system size dependence. The origin of this dependence is not in the self-interaction of a defect via the periodic boundary conditions but in the relaxation of the surrounding matrix from the ideal cubic structure to the distorted low-$T$ structure. The results for larger supercells considered ($N_{\text{vac}} = 16$–64) show that the presence of a defect causes only a very localized perturbation to the crystal structure and its charge-orbital order. This conclusion is confirmed by the absence of any significant system size dependence for the defect formation energies if $E_0$ of the low-$T$ phase is used as a reference (figure 8). This analysis of system size effects implies that the supercell of 56 atoms ($N_{\text{vac}} = 8$) is the best variant for the attempts to calculate using the static DFT + U method the point defect formation energies for the temperature stabilized cubic phase.

Liu and Di Valentin \([43]\) showed that releasing the symmetry constraint on the electron density but not the cubic phase geometry gives the charge disproportionation (Fe$^{2+}$/Fe$^{3+}$) and the small band gap for minority spin at the Fermi level that is consistent with several recent experiments \([65–68]\). In this work, we show that the semiconductor-like electronic structure of the cubic phase gives the total energy reference value $E_0$ resulting in $E_{\text{FP}}$ that agrees well with the experimental data. Using the cubic phase total energy from the DFT + $U$ calculation with symmetric electron density gives non-physical $E_{\text{FP}} < 0$. This is another quantitative argument in favor of semiconductor-like electronic structure of the cubic phase.

In this work, we report a refined value of 1.20 eV the B-vacancy formation energy that is lower than 1.26 eV obtained by us previously \([46]\). This fact suggests that the formation energies of other types of defects that we present could not be the lowest energies possible for each particular defect type. However, the energy steps between different types of interstitials in the energy hierarchy presented (see table 1) are significantly larger that the difference of 60 meV for $E_{\text{FP}}$. That is why one can expect this hierarchy is not sensitive to possible small corrections of defect energies and could be used for comparison with the experimental data available.

It was known for a long time from experiments that vacancies in magnetite are located predominantly on octahedral sites \([69]\). However, since defect formation energies in magnetite depend on oxygen activity, quantitative information on these energies is not easy to get experimentally. Such information became available from the experiments of Dieckmann \textit{et al} \([10–17]\). These experiments revealed that (a) the thermal point defect disorder of stoichiometric magnetite is of the Frenkel type and (b) despite of relatively high point defect concentrations, the point defects in magnetite form an ideal solution. Dieckmann \textit{et al} measured the temperature dependencies of the equilibrium constants $K_V$ and $K_I$ for the formation of cation vacancies and interstitials in the temperature range 900°C–1400°C. The product $K_VK_I$ is a FP equilibrium constant and its Arrhenius dependence on $1/T$ reveals two linear regimes with different slopes corresponding to two values of FP formation energies (see \([15]\)):

$$E_{\text{FP}} = 1.38 \text{ eV at } T < 1200 \text{°C and } E_{\text{FP}} = 3.11 \text{ eV at } T > 1300 \text{°C}.$$

Our DFT + $U$ data give the lowest FP formation energy for the pair of B-vacancy and B-interstitial $E_{\text{FP}} = 1.52$ eV (see table 2) that is only 10% higher than the experimental value. This agreement can be considered as a remarkable success of the DFT + $U$ model of the magnetite cubic phase for $U_{\text{eff}} = 3.5$ eV. As it is shown on figure 11, the agreement becomes even better for slightly higher values of $U_{\text{eff}}$. It is instructive to see how DFT + $U$ describes both quantitative parameters of the cubic phase considered: the band gap and the FP formation energy. Figure 11 shows that the best matching values of $U_{\text{eff}}$ for each property differ not very much. If we would prioritize the experimental data on the band gap (shown by the red background), then $E_{\text{FP}}$ is ~0.15 eV higher than the experimental value (for $U_{\text{eff}}$ shown by the green background). However, $E_{\text{FP}}$ (that is the sum of the B-vacancy and B-interstitial formation energies) would be somewhat lower if one takes into account the possibility to find even deeper energy minima and
Figure 10. 2 top pictures: the defect-free atomic structure and the B-vacancy atomic structure in supercells with 56(55) atoms after relaxation to the low-\(T\) phase. Three lower pictures: the structures of the B-vacancy in the supercells with 111, 223 and 447 atoms after relaxation to the low-\(T\) phase. The lines show the shortest distances between B-cations. Electron density distributions of the occupied \(t_{2g}\) orbitals of Fe\(^{2+}\) cations are shown by isosurfaces.

the possible influence of finite-\(T\) effects (i.e. the lattice dynamics). The opposite traverses of the \(E_g\) and \(E_{IP}\) dependencies on \(U_{\text{eff}}\) allow selecting an optimum range of \(U_{\text{eff}}\) on the basis of these two properties: the range \(U_{\text{eff}} = 3.4-3.6\) eV is expected to give the best overall description.

In this work, we use the effective \(U_{\text{eff}} = U-J\) following the approach of Dudarev et al [50]. Generally speaking, the value of \(U_{\text{eff}}\) is not universal: it depends on the type of chemical environment for a given element, on the basis used for Kohn–Sham orbitals representation, on the method of projection to localized orbitals. Using the low-\(T\) phase band gap as a reference, Pinto and Elliot [27] chose \(U_{\text{eff}} = 3.8\) eV in their study of magnetite within the very similar computational approach implemented in VASP (however they used the PW91 xc-functional and we use PBE). Jeng et al [28] used a similar approach as well but with the general form of the Hubbard correction \((U = 4.5\) eV, \(J = 0.89\) eV). Their choice of \(U\) was based on the band gap opening in the low-\(T\) phase too. Nowadays, there are advanced methods for calculations of Hubbard corrections from the first principles [49, 70, 71]. We are aware of
in supercells with 56 atoms (e.g. see figure 7). Therefore, our \textit{ab initio} results on point defects formation energies are expected to be applicable to high-$T$ conditions where, according to Dieckmann \textit{et al} point defects form an ideal solution.

An increase in the number of Fe$^{3+}$ cations and a decrease in the number of Fe$^{2+}$ cations in the case of a B-vacancy and an increase in the number of Fe$^{2+}$ cations and a decrease in the number of Fe$^{3+}$ cations in the case of a B-interstitial agree qualitatively with the experimental observations of Dieckmann \textit{et al} that divalent and trivalent cations serve to maintain electrical neutrality in the case of an interstitial and a vacancy, respectively.

Self-doping of stoichiometric magnetite via FP formation at temperatures up to 1200 K has been recently studied by Elnaggar \textit{et al} via core-level x-ray spectroscopy measurements \cite{9}. The authors discover that the asymmetrical broadening of the $K$ preedge peak can give information on a reordering of the Fe charges in magnetite. Using the ligand field multiplet calculations, the authors quantified the site occupation of Fe$^{3+}$ and Fe$^{2+}$ ions in octahedral and tetrahedral interstitial sites. The resulting model describing the $K$ preedge peak broadening is interpreted by Elnaggar \textit{et al} as the FP formation in magnetite via the cation exchange between octahedral and tetrahedral sublattices: Fe$^{2+}$ cations from octahedral sites fill neighboring tetrahedral sites and Fe$^{3+}$ cations from tetrahedral sites fill neighboring octahedral sites. Unfortunately, our results do not support this model: for the FP of B-vacancy with A2-interstitial $E_{\text{FP}} = 1.20 + 0.77 = 1.97$ eV, for the FP of A-vacancy with B-interstitial $E_{\text{FP}} = 2.50 + 0.32 = 2.82$ eV. Both values of $E_{\text{FP}}$ are significantly ($+0.45$ eV and $+1.3$ eV) higher than the value for the FP of B-vacancy with B-interstitial.

Using our results on the formation energies of vacancies and interstitials in the cubic phase of magnetite, we can discuss the high temperature FP formation energy value that can be deduced from the experimental data of Dieckmann \textit{et al} at $T > 1300$ K \cite{15}: $E_{\text{FP}} = 3.11$ eV. The corresponding best selection from the individual formation energies of a vacancy and an interstitial is a pair of A-vacancy and A2-interstitial that gives $E_{\text{FP}} = 2.50 + 0.77 = 3.27$ eV (only 5\% higher than the experimental value). This fact suggests the following interpretation of the experimental data \cite{15} on the Arrhenius dependencies for the equilibrium constants of point defect formation: at lower $T$ the activation energy is determined by the FP formation in the B-sublattice and at higher $T$ the FP formation in A-sublattice is the main mechanism. However, the equilibrium constants have thermodynamic meaning only and tell us nothing about possible mechanisms of FP formation that is why the comparison of our interpretation for the experiments of Dieckmann \textit{et al} with the results of Elnaggar \textit{et al} \cite{9} and their interpretation require further studies.

Here it is worth noticing that the study of tetrahedral interstitial atoms is greatly hindered by the fact that they form complexes in small supercells due to the fact that their formation in interstitials of small volume causes large distortions. At the same time, large supercells will again be characterized by a mixture of the effects of local relaxation due to a defect and global defect-free relaxation.
5. Conclusions

The DFT + U model of magnetite crystal has been considered for the supercells with 56–448 atoms and one pattern of Verwey-type charge-orbital ordering that corresponds to the kind of the lowest energy self-consistent DFT + U solutions for magnetite electronic structure. The ideal cubic and the distorted low-\(T\) defect-free structures have been considered as the references for studying point defects. In the latter case, the chains of trimeron-like atomic distortions coupled to the charge-orbital ordering pattern have been observed. The hierarchy of the interstitials formation energies has been calculated and the previously found [46] formation energy for the octahedral vacancy has been refined. It has been shown that the octahedral vacancy and the octahedral interstitial have the lowest formation energies among cation point defects.

The semiconductor-like small gap electronic structure of the reference state (obtained without imposing crystal symmetry constraints on electronic density) gives adequate point defect formation energies. The semi-metallic reference state (obtained with electronic density symmetrization) should be disqualified since it results in negative point defect formation energies.

It has been shown for the larger system sizes that the atomic relaxation of defective structures in addition to relaxation associated with defect formation includes also the regular cubic phase distortions leading the atomic structure towards the low-\(T\) phase. The contribution of these regular distortions to the total energy change during relaxation is proportional to the system size and becomes larger for larger supercells. At the same time, point defects cause very localized perturbations in magnetite crystal structure and its charge-orbital ordering. That is why the smallest 56 atom supercell is the best choice for the static DFT + U calculation of defect formation energies in the temperature stabilized cubic phase. In this case the relaxation of defective structure is not affected by the relaxation of the surrounding crystal matrix.

The lowest calculated cation FP formation energy 1.52 eV \((U_{\text{eff}} = 3.5 \text{ eV})\) found for the pair of an octahedral vacancy and an octahedral interstitial is in a good agreement with the value of 1.38 eV deduced from the equilibrium constant of FP formation based on the experimental data of Dieckmann \textit{et al} for \(T < 1200 \, ^\circ\text{C}\) [15]. It has been shown that the increase of \(U_{\text{eff}}\) results in the smaller octahedral FP formation energy \(E_{\text{FP}}\) while the energy gap \(E_g\) in the cubic phase increases. The best match for \(E_{\text{FP}}\) and for \(E_g\) to experimental data can be found for nearly the same magnitude of the Hubbard \(U_{\text{eff}}\) correction.

We have noticed that the FP formation energy of 3.11 eV deduced from the experimental data of Dieckmann \textit{et al} for \(T > 1300 \, ^\circ\text{C}\) [15] corresponds quite well to our result of 3.27 eV for the formation energy of the cation FP comprised of a tetrahedral vacancy and a tetrahedral interstitial.

Unfortunately, the hierarchy of point defects and FPs formation energies based on our DFT + U data does not support the model of the Frenkel disorder in stoichiometric magnetite at high temperatures that was proposed by Elnaggar \textit{et al} for the interpretation of their core-level x-ray spectroscopy measurements [9]. That model was based on the assumption of the formation of the mixed FPs comprised of an octahedral vacancy with a tetrahedral interstitial and a tetrahedral vacancy with an octahedral interstitial. In our model, the formation energies for these FPs are \(+0.45 \text{ eV}\) and \(+1.3 \text{ eV}\) higher than the formation energy of the octahedral FP.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors. DOI: 10.1088/1742-6596/1740/1/012050.

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References

[1] Verwey E 1939 \textit{Nature} \textbf{144} 327–8
[2] Walz F 2002 \textit{J. Phys.: Condens. Matter} \textbf{14} R285–340
[3] Garcia J and Subias G 2004 \textit{J. Phys.: Condens. Matter} \textbf{16} R145
[4] Senn M, Wright J and Attfield J 2012 \textit{Nature} \textbf{481} 173–6
[5] Attfield J P 2022 \textit{Chem. Mater.} \textbf{34} 2877–85
[6] Perversi G, Pachoud E, Cumby J, Hudspeth J M, Wright J P, Kimber S A J and Attfield P J 2019 \textit{Nat. Commun.} \textbf{10} 2857
[7] Elnaggar H \textit{et al} 2020 \textit{Phys. Rev. B} \textbf{101} 085107
[8] Momma K and Izumi F 2011 \textit{J. Appl. Crystallogr.} \textbf{44} 1272–6
[9] Elnaggar \textit{et al} 2021 \textit{Phys. Rev. Lett.} \textbf{127} 186402
[10] Dieckmann R and Schmalzried H 1977 \textit{Ber. Bunsenges. Phys. Chem.} \textbf{81} 414–9
[11] Dieckmann R and Schmalzried H 1977 \textit{Ber. Bunsenges. Phys. Chem.} \textbf{81} 344–7
[12] Dieckmann R, Mason T O, Hodge J D and Schmalzried H 1978 \textit{Ber. Bunsenges. Phys. Chem.} \textbf{82} 778–83
[13] Dieckmann R 1982 \textit{Ber. Bunsenges. Phys. Chem.} \textbf{86} 112–8
[14] Dieckmann R, Witt C A and Mason T O 1983 \textit{Ber. Bunsenges. Phys. Chem.} \textbf{87} 495–503
[15] Dieckmann R and Schmalzried H 1986 \textit{Ber. Bunsenges. Phys. Chem.} \textbf{90} 564–75
[16] Dieckmann R, Hilton M R and Mason T O 1987 \textit{Ber. Bunsenges. Phys. Chem.} \textbf{91} 59–66
[17] Dieckmann R 1998 \textit{J. Phys. Chem. Solids} \textbf{59} 507–25
[18] Yanase A and Siratori K 1984 \textit{J. Phys. Soc. Japan} \textbf{53} 312–7
[19] Zhang Z and Satpathy S 1991 \textit{Phys. Rev. B} \textbf{44} 13319–31
[20] Anisimov V I, Efimov I S, Hamada N and Terakura K 1996 Phys. Rev. B 54 4387–90
[21] Hendy S, Walker B, Laycock N and Ryan M 2003 Phys. Rev. B 67 085407
[22] Jeng H, Guo G Y and Huang D J 2004 Phys. Rev. Lett. 93 156403
[23] Leonov I, Yaresko A N, Antonov V N, Korotin M A and Anisimov I V 2004 Phys. Rev. B 70 144604
[24] Craco L, Laad M S and Muller-Hartmann E 2006 Phys. Rev. B 74 064425
[25] Leonov I V, Yaresko A N, Antonov V N and Anisimov V I 2006 Phys. Rev. B 74 165117
[26] Piekarsz P, Parlinski K and Oles A M 2006 Phys. Rev. Lett. 97 156402
[27] Pinto H P and Elliott S D 2006 J. Phys.: Condens. Matter 18 104276–37
[28] Jeng H T, Guo G and Huang D 2006 Phys. Rev. B 74 195115
[29] Piekarsz P, Parlinski K and Oles A M 2007 Phys. Rev. B 76 165124
[30] Wenzel M J and Steinle-Neumann G 2007 Phys. Rev. B 75 214430
[31] Rowan A D, Patterson C H and Gasparov L V 2009 Phys. Rev. B 79 205103
[32] Yamauchi K, Fukushima T and Picciorzi S 2009 Phys. Rev. B 79 212404
[33] Arras R, Calmels L and Warot-Fonrose B 2010 Phys. Rev. B 81 104422
[34] Zhou F and Ceder G 2010 Phys. Rev. B 81 205113
[35] Fukushima T, Yamauchi K and Picciorzi S 2011 J. Phys. Soc. Japan 80 014709
[36] Arras R, Calmels L and Warot-Fonrose B 2012 Appl. Phys. Lett. 100 032403
[37] Senn M S, Loa I, Wright J P and Attfield J P 2012 Phys. Rev. B 85 125119
[38] Arras R, Warot-Fonrose B and Calmels L 2013 J. Phys.: Condens. Matter 25 256002
[39] Noh J, Osman O, Aziz S, Winget P and Bredas J 2014 Sci. Technol. Adv. Mater. 15 044202
[40] Li D, Qu B, He H, Zhang Y, Xu Y, Pan B and Zhou R 2016 Phys. Chem. Chem. Phys. 18 7789–96
[41] Muhlich C L, Aston V J, Trottier R M, Weimer A W and Musgrave C B 2016 Chem. Mater. 28 214–26
[42] Meng Y et al 2016 J. Chem. Theory Comput. 12 5132–44
[43] Liu H and Di Valentino C 2017 J. Phys. Chem. C 121 25736–42
[44] Liningor C, Cana C, Takeuchi K, Marschikol A, Takeuchi E, West A and Hybertsen M 2018 Chem. Mater. 30 7922–37
[45] Piekarsz P et al 2021 Phys. Rev. B 103 104303
[46] Shutikova M I and Stegailov V V 2021 J. Exp. Theor. Phys. 133 206–28
[47] Anisimov V I, Zaanen J and Andersen O K 1991 Phys. Rev. B 44 943
[48] Anisimov V I, Arysaeiwan F and Lichtenstein A I 1997 J. Phys.: Condens. Matter 9 767–808
[49] Cococcioni M and de Gironcoli S 2005 Phys. Rev. B 71 035105
[50] Dudarev S L, Botton G A, Savrasov S Y, Humphreys C J and Sutton A P 1998 Phys. Rev. B 57 1505–9
[51] Kresse G and Hafner J 1993 Phys. Rev. B 47 558–61
[52] Kresse G and Furthmüller J 1996 Phys. Rev. B 54 11169–86
[53] Stegailov V, Smirnov G and Vecher V 2019 Concurr. Comput. Pract. Exp. 31 e5136
[54] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[55] Okadera H, Kihara K and Matsumoto T 1996 Acta Crystallogr. B 52 450–7
[56] Streltsov S V, Ryltsev R E and Chtkelkatchev N M 2022 J. Alloys Compd. 912 165150
[57] Freysoldt C, Grabowski B, Hickel T, Neugebauer J, Kresse G, Janotti A and Van de Walle C G 2014 Rev. Mod. Phys. 86 253–305
[58] Kagan M Y, Kugel K and Rakhmanov A 2021 Phys. Rep. 916 1–105
[59] Orlov Y S, Daudhikov V, Sokolov A, Ovchinnikova T, Shestakov N and Ovchinnikov S 2022 JETP Lett. 115 615–9
[60] Doltsinis N L and Marx D 2002 Phys. Rev. Lett. 88 166402
[61] Stegailov V and Zhilayeva P 2016 Mol. Phys. 114 509–18
[62] Smith B and Akimov A V 2019 J. Phys.: Condens. Matter 32 073001
[63] Fedorov I D, Orekhov N D and Stegailov V V 2020 Phys. Rev. B 101 100101
[64] Zhang L, Chu W, Zhao C, Zheng Q, Prezhdo O V and Zhao J 2021 J. Phys. Chem. Lett. 12 2191–9
[65] Park J H, Tjeng I H, Allen J W, Metcalf P and Chen C T 1997 Phys. Rev. B 55 12813–7
[66] Schnupp D, Sing M, Tsunekawa M, Fujiwara H, Kasai S, Sekiyama A, Suga S, Muro T, Brabers V and Claessen R 2005 Europhys. Lett. 70 789
[67] Hevorni A, Bapna M, Piotrowski S, Majetic S A and Markovich G 2016 J. Phys. Chem. Lett. 7 1661–6
[68] Banerjee A and Pal A 2020 J. Phys.: Condens. Matter 32 055701
[69] Daniels J and Rosencwaig A 1969 J. Phys. Chem. Solids 30 1561–71
[70] Timrov I, Marzari N and Cococcioni M 2018 Phys. Rev. B 98 085127
[71] Timrov I, Marzari N and Cococcioni M 2021 Phys. Rev. B 103 045141
[72] Voss J 2022 J. Phys. Commun. 6 035009
[73] Chernov E, Lukoyanov A and Anisimov V 2021 J. Exp. Theor. Phys. 132 548–55
[74] Eglitis R I, Purans J, Gabrusenoks J, Popov A I and Jia R 2020 Crystals 10 745
[75] Eglitis R I, Purans J, Popov A I, Bocharov D, Chekhovska A and Jia R 2022 Symmetry 14 1050