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Calculation of cohesive energy of Ti_4O_7

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The cohesive energy of Ti_4O_7 cannot be determined experimentally by a Born–Haber cycle analysis because the heat of formation of this compound, one of the energies associated with steps involved in the cycle, has not been obtained experimentally. Therefore, this paper reports the calculation of the cohesive energy of Ti_4O_7 based on the real structure observed at 120 K by X-ray diffraction. The cohesive energy consists of the Madelung energy calculated by Ewald's method, the repulsive energy, van der Waals's energy, the zero-point energy and the energy associated with bipolarons formed in Ti_4O_7 at temperatures below 150 K. The calculated value for the cohesive energy is −390.26 eV per Ti_4O_7 "molecule". This value is found to be nearly equal to the upper limit of the cohesive energy of the Ti_4O_7 "molecule" which is approximately estimated by extrapolating the experimental results for the heats of formation of TiO_2 and Ti_3O_5 in Born–Haber cycle analyses.

1. Introduction

It is well known that if rutile (TiO_2) is reduced to compositions down to approximately $TiO_{1.998}$, the change in anion to cation stoichiometry is accounted for by the formation of crystallographic shear (CS) planes [1, 2]. At greater degrees of reduction, between the limits $TiO_{1.66}$ and $TiO_{1.90}$ an homologous series of oxides with the formula (Ti_nO_{2n-1}) forms, with n taking values from 4 to 9 or 10, in which CS planes lie upon $\{1\,2\,1\}$ plains. The oxide Ti_4O_7 (i.e. n in $Ti_nO_{2n-1} = 4$) is said to be the most stable phase in this homologous series.

In addition, Ti_4O_7 has received increasing attention in recent years because of its physical characteristics. The oxide is a good electric conductor at room temperature, being metallic, but exhibits a metal–semiconductor transition at 150 K on cooling. The crystal structure of Ti_4O_7 has been studied extensively as a function of temperature using X-ray diffraction methods, in order to clarify the correlation between its behaviour and the structure [3–7]. These studies have shown that at room temperature the effective charge on the titanium atoms is +3.5 and that this is evenly distributed over every metal atom in the structure. On cooling to 120 K, however, a segregation into Ti^{3+} and Ti^{4+} ions occurs, and Ti^{3+} ions are located at the sites adjacent to CS planes. These Ti^{3+} ions make Ti^{3+}–Ti^{3+} pairs called dimers, and pairs of electrons trapped on these Ti^{3+} ions form bipolarons, creating a local deformation of the lattice which is observable by X-ray diffraction [5, 8, 9]. The bipolarons are also shown to exist in Ti_4O_7 below the transition temperature by specific heat measurements and EPR [8].

In order to investigate such interesting properties, we need, for both experimental and theoretical studies, the cohesive energy, which is one of the fundamental material constants. Wackman *et al.* [10] have calculated the value for the cohesive energy of TiO_2 (rutile) which is found to nearly coincide with the experimental value obtained by using Born–Haber cycle analysis. In this paper, using their approach, we will calculate the cohesive energy of Ti_4O_7, the structure of which has been characterized by X-ray diffraction [5], and also compare the evaluated value with the value estimated experimentally. In determining the cohesive energy of Ti_4O_7 by a Born–Haber cycle analysis, however, one of the experimental values involved in this cycle is not yet available. Nevertheless we can estimate the experimental value for the cohesive energy of Ti_4O_7, but with a large error. Considering these situations, it is worth calculating the cohesive energy of Ti_4O_7 theoretically. In this report, we have calculated the Madelung energy and the repulsive energy, the dominant parts in the cohesive energy, in the same way as described in our previous reports [11, 12], which is quite different from the way in which these energies were calculated by Wackman *et al.* [10].

2. Calculations and results

2.1. Crystal structure of Ti_4O_7

The calculation of the cohesive energy requires that the structure of crystals at low temperatures (if available, at 0 K) is known. The crystal structure of Ti_4O_7 depends on temperature and, as described in Section 1, it has been investigated extensively as a function of temperature by X-ray diffraction methods, because Ti_4O_7 shows a semiconductor–metal transition at 150 K on cooling. Our calculation is based upon the X-ray diffraction data of the Ti_4O_7 structure measured at 120 K by Marezio *et al.* [5] because these data are the ones which were obtained at the lowest temperature to date.

The crystal structure of Ti_4O_7 is related to that of rutile (TiO_2) and consists of rutile-like blocks which are infinite in two dimensions and four oxygen octahedra wide in the third dimension. Along the plane

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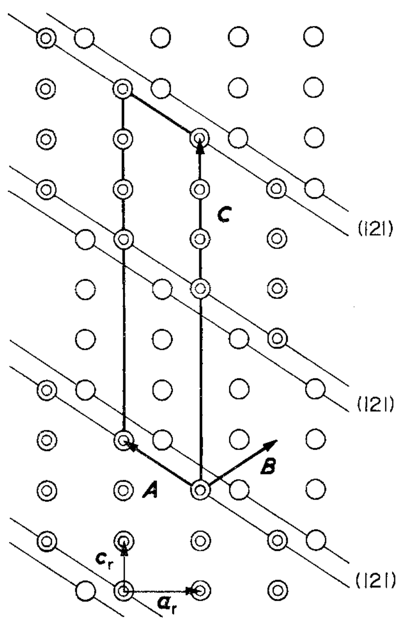

Figure 1 Titanium sites on the {0 1 0} planes of the Ti_4O_7 structure. The open circles represent Ti^{4+} ions and the double ones Ti^{3+} ions. The double lines which link the centres of circles represent the cores of {1 2 1} CS planes. The vectors, A and C, lie in the {0 1 0} planes and the projection of the vector $\boldsymbol{B}$ upon the {0 1 0} plane is indicated. The primitive unit cell used in the calculations is heavily outlined. The unit vector $\boldsymbol{a}_r$ and $\boldsymbol{c}_r$ along the pseudorutile *a*- and *c*-axes of the unit cell are also shown. Oxygen sites are omitted in this figure.

separating these blocks ({1 2 1} CS planes), the octahedra share faces, edges and corners, while inside the blocks they share only edges and corners. The oxygen-ion packing remains essentially closed packed. The structure with four different crystallographic sites may be viewed as containing two types of titanium chains, running parallel to the pseudorutile *c*-axis and truncated every four titanium sites by CS planes.

According to the X-ray diffraction data [5], below the transition temperature the charges on cation sites are found to be localized into alternate chains of +3 sites paired to form bipolarons. We have shown the distribution of titanium sites in the Ti_4O_7 structure on {0 1 0} planes in Fig. 1. Single open circles indicate Ti^{4+} ions and the double ones represent Ti^{3+} ions; the double lines which link centres of circles are the {1 2 1} CS planes. In Fig. 1, for references, the unit vector $\boldsymbol{a}_r$ and $\boldsymbol{c}_r$ along the pseudorutile *a*- and *c*-axes of the tetragonal unit cell are shown. Along the *b*-axis normal to *a*- and *c*-axes, the tetragonal rutile unit cell has a unit vector $\boldsymbol{b}_r$ the absolute value of which is the same as that of $\boldsymbol{a}_r$. In this figure, oxygen sites are omitted.

The structure of crystals such as Ti_4O_7 is constructed by the formal geometrical translocation vector $\boldsymbol{R}_n$ [13],

$$\boldsymbol{R}_n = n_1\boldsymbol{A} + n_2\boldsymbol{B} + n_3\boldsymbol{C} \tag{1}$$

where n_1, n_2 and n_3 are integers and the vectors $\boldsymbol{A}$, $\boldsymbol{B}$, and $\boldsymbol{C}$ are expressed by linear combinations of vectors $\boldsymbol{a}_r$, $\boldsymbol{b}_r$ and $\boldsymbol{c}_r$ in the following way [6],

$$\begin{aligned} \boldsymbol{A} &= -\boldsymbol{a}_r + \boldsymbol{c}_r \\ \boldsymbol{B} &= \boldsymbol{a}_r - \boldsymbol{b}_r + \boldsymbol{c}_r \\ \boldsymbol{C} &= 7\boldsymbol{c}_r \end{aligned} \tag{2}$$

In Fig. 1, the projections of vectors $\boldsymbol{A}$, $\boldsymbol{B}$ and $\boldsymbol{C}$ on the {0 1 0} plane and their origin are indicated. The primitive unit cell of Ti_4O_7 constructed with these vectors contains, as shown in Fig. 1, two {1 2 1} CS planes.

Andersson and Jahnberg [14] constructed the triclinic CS unit cell with the vectors $\boldsymbol{a}_a$, $\boldsymbol{b}_a$ and $\boldsymbol{c}_a$. Using these vectors, the positions of the *j*th ion in the unit cell of Ti_4O_7 is given as follows

$$\boldsymbol{r}_j = x_a\boldsymbol{a}_a + y_a\boldsymbol{b}_a + z_a\boldsymbol{c}_a \tag{3}$$

where (x_a, y_a, z_a) are the co-ordinates of the *j*th ion represented in units of the triclinic vectors $\boldsymbol{a}_a$, $\boldsymbol{b}_a$ and $\boldsymbol{c}_a$ [5–7]. Marezio *et al.* [5] report the X-ray diffraction data for the co-ordinates (x_a, y_a, z_a) of every ion in the unit cell of Ti_4O_7 at 120 K. In simplifying the calculation of the cohersive energy, however, the co-ordinates of each ion site expressed in units of the tetragonal unit vectors $\boldsymbol{a}_r$, $\boldsymbol{b}_r$ and $\boldsymbol{c}_r$ are much better. Using the following relations, Equation 4, we have translated the co-ordinates of the *j*th ion site from the triclinic system to the tetragonal one.

$$\begin{aligned} \boldsymbol{a}_a &= -\boldsymbol{a}_r + \boldsymbol{c}_r \\ \boldsymbol{b}_a &= \boldsymbol{a}_r - \boldsymbol{b}_r + \boldsymbol{c}_r \\ \boldsymbol{c}_a &= \boldsymbol{a}_r + 2\boldsymbol{b}_r + 2\boldsymbol{c}_r \end{aligned} \tag{4}$$

In Equation 4, we have taken the direction of $\boldsymbol{b}_r$ along the opposite direction employed by Andersson and Jahnberg [14]. The lattice site of the *j*th ion $\boldsymbol{r}_j$ translated to the tetragonal system is then written,

$$\begin{aligned} \boldsymbol{r}_j &= (-x_a + y_a + z_a)\boldsymbol{a}_r + (-y_a + 2z_a)\boldsymbol{b}_r \\ &\quad + (x_a + y_a + 2z_a)\boldsymbol{c}_r \\ &= x_r\boldsymbol{a}_r + y_r\boldsymbol{b}_r + z_r\boldsymbol{c}_r \end{aligned} \tag{5}$$

where (x_r, y_r, z_r) are the tetragonal co-ordinates of the *j*th ion and we have used these co-ordinates for the ion sites in calculating the cohesive energy.

2.2. Calculations

Referring to Wackman *et al.* [10], the cohesive energy in Ti_4O_7 consists of five terms, i.e.

$$U = U_1 + U_2 + U_3 + U_4 + U_5 \tag{6}$$

The first term, U_1, is the Madelung energy which is the sum of coulombic interaction energies between ions. U_2 is the repulsive energy which is represented in the form of a Born–Mayer potential and U_3 is the van der Waals's energy. The energy U_4 is the zero-point energy. Finally, U_5 is the energy associated with the formation of bipolarons.

The Madelung energy of each ion in a crystal is obtained, in general, by using Ewald's method [15] and, in this report, so as to calculate Madelung energies, we have employed the self potentials which are developed from Ewald's method by Van Gool and Piken [16]. Then the Madelung energy per Ti_4O_7 "molecule" has the form

$$U_1 = (1/4)\left\{(1/2)\sum_{i}^{\text{u.c.}} q_i\Phi_i(0)\right\} \tag{7}$$

where $q_i\Phi_i(0)$ indicates the Madelung energy of the *i*th ion with charge q_i, $\Phi_i(0)$ being the self potential of the

TABLE I The parameters used in the repulsive energy and van der Waals's energy

	A_{ij}(eV)	B_{ij} (nm^{-1})	C_{ij} ($\mathrm{eV\,nm}^{-6} \times 10^{-7}$)
Ti^{4+}–Ti^{4+}	9.557×10^{3}	54.08	−1.8847
Ti^{4+}–O^{2-}	1.164×10^{3}	30.35	−1.1998
O^{2}–O^{2-}	1.597×10^{5}	66.09	−2.2987
Ti^{3+}–Ti^{3+}	1.934×10^{4}	54.08	−1.8847
Ti^{3+}–Ti^{3+}	1.361×10^{4}	54.08	−1.8847
Ti^{3+}–O^{2-}	1.418×10^{3}	30.35	−1.1998

TABLE II The Madelung energy U_1, the repulsive energy U_2, van der Waals's energy U_3, the zero-point energy U_4, the energy associated with bipolarons U_5, and the cohesive energy $U(Ti_4O_7)$. Every energy is expressed in units of eV per Ti_4O_7 "molecule".

Madelung energy (U_1)	−465.000
Repulsive energy (U_2)	83.309
Van der Waals's energy (U_3)	−8.630
Zero-point energy (U_4)	0.526
Polaron energy (U_5)	−0.460
Cohesive energy ($U(Ti_4O_7)$)	−390.255

ith ion (see [16]), and $\Sigma_i^{\mathrm{u.c.}}$ represents the summation of Madelung energies of all ions in the unit cell. The numerical factors (1/2) and (1/4) come in Equation 7 because all pairwise interactions are counted twice in $\Sigma_i^{\mathrm{u.c.}}\ q_i\Phi_i(0)$ and one unit cell, as indicted in Fig. 1, contains four Ti_4O_7 "molecules". In this paper, we have employed the following lattice constants [11, 12],

$$|\boldsymbol{a}_{\mathrm{r}}| = |\boldsymbol{b}_{\mathrm{r}}| = 0.459\,37\,\mathrm{nm}, |\boldsymbol{c}_{\mathrm{r}}| = 0.295\,81\,\mathrm{nm}$$

The repulsive energy per Ti_4O_7 "molecule", U_2, has, as described before, a form of a Born–Mayer potential which was employed in our previous reports [11, 12],

$$U_2 = (1/2)\sum_{i}^{\mathrm{u.c.}}\left\{\sum_{j\neq i} A_{ij}\exp\left(-B_{ij}r_{ij}\right)\right\} \qquad (8)$$

where $\{\Sigma_{j\neq i}A_{ij}\exp(-B_{ij}r_{ij})\}$ represents the repulsive energy of the ith ion which interacts with all of other ions in the crystal and r_{ij} is the spacing between the ith and jth ions. The van der Waals's energy per Ti_4O_7 molecule has the following form which is the same as used in our previous calculations [11, 12],

$$U_3 = (1/2)\sum_{i}^{\mathrm{u.c.}}\left\{\sum_{j\neq i} C_{ij}/r_{ij}^{6}\right\} \qquad (9)$$

where C_{ij} is the van der Waals's constant between the ith and jth ions. In Equations 8 and 9, the numerical factor (1/2) appears for the same reason as in Equation 7. In the present calculation, we have used the same parameters for the Born–Mayer potentials (A_{ij} and B_{ij}) and the van der Waals's contant (C_{ij}) as used in our previous reports [11, 12]. Since Ti_4O_7 is a mixed valence compound with as many Ti^{3+} ions as Ti^{4+} ions, and the repulsive energy is likely to be sensitive to charges on ions as well as the Madelung energy, the parameters for the Born–Mayer potentials involving trivalent cations are obtained by a scaling procedure based on ionic radii [17]. For this, the ionic radii of Ti^{4+} and Ti^{3+} ions have been taken as 0.0605 and 0.0670 nm, respectively [18]. By using the parameters given in Table I, these energies based on the real structure of Ti_4O_7 have been calculated and are shown in Table II along with other energies.

The zero-point energy per Ti_4O_7 "molecule", U_4, is calculated in the same way as Wackman *et al.* [10], i.e.

$$U_4 = 9nh\nu_{\mathrm{max}/8} \qquad (10)$$

where n is the number of ions per Ti_4O_7 "molecule", i.e. n being 11, h is Planck's constant and ν_{max} is the Debye limiting frequency. According to specific-heat measurements by Lakkis *et al.* [8], the heat capacity at constant pressure between 10 and 40 K is found to follow Debye's law, (a T^3 law), with Debye temperature, θ_{D}, of (493 ± 10) K. Using the following relation between the Debye limiting frequency and the Debye temperature [19],

$$\nu_{\mathrm{max}} = (k/h)\theta_{\mathrm{D}} \qquad (11)$$

we have obtained a value $\nu_{\mathrm{max}} = 1.03 \times 10^{13}\,\mathrm{sec}^{-1}$ where k is Boltzmann's constant. Then we find $U_4 = 0.526\,\mathrm{eV}/Ti_4O_7$ "molecule".

As described before, Ti_4O_7 contains Ti^{3+}–Ti^{3+} pairs called dimers. According to to the EPR results obtained by Lakkis *et al.* [8], the ground level of Ti^{3+} ions is lower than that of Ti^{4+} ions by ~ 0.08 eV. In addition, the ground state of Ti^{3+} ions is lowered further by ~ 0.15 eV due to the spin–spin interaction between electrons trapped on Ti^{3+}–Ti^{3+} pairs. Consequently, Ti^{3+} ions in Ti_4O_7 have an energy level lower than that of Ti^{4+} ions by ~ 0.23 eV. As one Ti_4O_7 "molecule" has two Ti^{3+} ions, the energy associated with the formation of bipolarons, U_5, is found to be about −0.46 eV per Ti_4O_7 "molecule".

The summation of these energies, as discussed above, allows us to find the cohesive energy per Ti_4O_7 "molecule" to be $U(Ti_4O_7) = -390.26\,\mathrm{eV}$. As a Ti_4O_7 "molecule" contains four $TiO_{1.75}$, the cohesive energy per $TiO_{1.75}$ has a value of −97.57 eV.

3. Discussion

The cohesive energy can be determined experimentally by a Born–Haber cycle analysis [10]. In this method, we have to consider all the steps involved in transforming four titanium metal atoms and three and one-half (7/2) oxygen gas atoms to one Ti_4O_7 "molecule", that is,

$$4\mathrm{Ti(solid)} + (7/2)\mathrm{O_2(gas)} \rightarrow \mathrm{Ti_4O_7(solid)} \qquad (12)$$

The energy associated with each step of this cycle can be determined from thermochemical data, if they are available. In the case of Ti_4O_7, then, the formula for the cohesive energy is given as follows,

$$U = \Delta H_{\mathrm{O}} - 4L - (7/2)D_{\mathrm{O_2}} + 7A - 2(I_3 + I_4) \qquad (13)$$

where ΔH_{O} is the heat of the formation of Ti_4O_7, L is the heat of vaporization of titanium metal, $D_{\mathrm{O_2}}$ is the dissociation energy of the O_2 gas, A is the affinity of the oxygen atoms for two electrons and I_4 and I_3 are the sums of the first four and the first three ionization potentials of the titanium atom, respectively. The last term $2(I_4 + I_3)$ is included in Equation 13 because a Ti_4O_7 "molecule" has two Ti^{4+} ions and also two Ti^{3+}

ions. Every value of these thermochemical data except the heat of the formation of Ti_4O_7 (ΔH_O) has been obtained experimentally. Rossini *et al.* [20] report $L = 4.38$ eV which is quite close in value to 4.36 eV quoted in the *American Institute of Physics Handbook* [21]. As for the dissociation energy for the oxygen (D_{O_2}), we have two data which are also very close in value, one is 5.116 eV obtained by Stull [22] and the other is 5.085 eV reported by Cottrell [23]. Various values for the affinity of two electrons (A) have appeared in the literature, e.g. Sherman [24] reports $A = -7.289$ eV, Ladd and Lee [25] report $A = -7.765$ eV, Huggins and Sakamoto [26] report $A = -(7.679$ to $\sim 6.377)$ eV. We have used the following values for the ionization potentials of the titanium atom, $I_4 = 91.157$ eV and $I_3 = 47.891$ eV [27]. Therefore, the cohesive energy per Ti_4O_7 "molecule", $U(Ti_4O_7)$, determined experimentally lies in the range, i.e. $\Delta H_O - 4 \times 4.38 - (7/2) \times 5.12 - 7 \times 7.77 - 2 \times (91.157 + 47.891) \leqq U(Ti_4O_7) \leqq \Delta H_O - 4 \times 4.36 - (7/2) \times 5.09 - 7 \times 6.38 - 2 \times (91.157 + 47.891)$, that is,

$$\Delta H_O - 367.93\,(\mathrm{eV}) \leqq U(Ti_4O_7) \leqq \Delta H_O - 358.01\,(\mathrm{eV}) \qquad (14)$$

As shown in Equation 14, in order to determine the value for the cohesive energy finally, we need the heat of the formation of Ti_4O_7 which, unfortunately, we have not yet obtained experimentally. Although Merritt *et al.* [28] measured the free energy of the Ti–O binary system in the range of $1.75 \leqq x$ in $TiO_x \leqq 2.00$ at 1304 K, we cannot estimate the value of ΔH_O of Ti_4O_7 from their experimental data. Picard and Gerdanian [29] also investigated experimentally the thermodynamics of TiO_x, but x in TiO_x in their experiments is less than 0.012, i.e. their samples are closer to TiO_2 than Ti_4O_7. Therefore, we cannot use their results in our calculations. However, we have thermochemical data for ΔH_O of several compounds in the Ti–O binary system [27], e.g. ΔH_O per TiO_2 "molecule" $= -9.907$ eV, ΔH_O per Ti_3O_5 "molecule" $= -25.509$ eV and ΔH_O for $Ti_2O_3 = -15.647$ eV. The heats of formation per TiO_x are, then, -9.907 eV for TiO_2, -8.503 eV for $TiO_{1.67}$ and -7.824 eV for $TiO_{1.5}$. Thus the heat of formation per TiO_x "molecule" is found to increase as x in TiO_x decreases. From this relationship, the heat of formation per Ti_4O_7 "molecule" would appear to be in the range of $4 \times (-9.907) = -39.63$ eV to $(4/3) \times (-25.509) = -34.01$ eV because a Ti_4O_7 "molecule" contains four $TiO_{1.75}$ "molecule". Using this the value for $U(Ti_4O_7)$ lies in the following energy range,

$$-407.56\,(\mathrm{eV}) < U(Ti_4O_7) < -392.02\,(\mathrm{eV}) \qquad (15)$$

Though our calculated value for $U(Ti_4O_7)$, -390.26 eV, is not in the energy range of Equation 15, it is nearly equal to the upper limit of $U(Ti_4O_7)$ given in Equation 15. According to the discussion above, the cohesive energy per TiO_x would appear to increase smoothly as the decrease in x. If the cohesive energy of Ti_4O_7 could be determined by a Born–Haber cycle analysis, then, it would be close in value to the upper limit in Equation 15, i.e. -392.02 eV, which shows a high possibility that the cohesive energy of Ti_4O_7 estimated in this calculation has the value quite near to the experimental one. This fact supports the validity of our calculations.

James and Catlow [30], on the other hand, report that the lattice energy per Ti_4O_7 "molecule" at 298 K is -344.62 eV. According to their calculations, their lattice energy appears to include the Madelung energy, the repulsive energy and the van der Waals's energy which have been calculated for the real structure of Ti_4O_7. Besides these energies, we have evaluated the zero-point energy and also the energy associated with bipolarons which are, as shown in Table II, very small compared with other energies and, therefore, their lattice energy does not change much even if the zero-point energy and the energy associated with bipolarons are involved in their calculations. Their lattice energy, therefore, seems to deviate from not only the cohesive energy estimated experimentally by using a Born–Haber cycle analysis but also our calculated value.

In our series of energy calculations for the Ti–O binary system [12, 13, 31], we have used a fully ionic model although some covalent contribution is presented [32]. The comparison of our calculated value and the experimental one for the cohesive energy of Ti_4O_7 leads to a conclusion that the bonding in the Ti–O system is predominantly ionic.

The parameters for the Born–Mayer potentials and the van der Waals's interactions used in our calculations are determined from experimental data such as the bulk modulus, elastic constants [32] and the cohesive energy of stoichiometric rutile (TiO_2) [10, 11]. The agreement between the calculated cohesive energy and the experimental one, as discussed above, indicates that these parameters also hold for each ion in Ti_4O_7. This fact suggests that physical and chemical properties of titanium ions and oxygen ions are essentially structure-independent in the Ti–O binary system. This suggestion indicates a possibility that material constants such as the bulk modulus and elastic constants of Ti_4O_7 estimated theoretically by using these parameters are expected to be not too far from experimental ones should they be measured in the future.

We have worked on energy calculations of TiO_2 [11], $Ti_{20}O_{39}$ based on the ideal structure [12] and Ti_4O_7 in this report. The cohesive energy per TiO_2 "molecule" is -124.3 eV. For $Ti_{20}O_{39}$, the summation of the Madelung energy, the repulsive energy and the van der Waals's energy, is found to be -2380.62 eV per $Ti_{20}O_{39}$ "molecule". If we assume the same value for the Debye limiting frequency as that of TiO_2, the zero-point energy of $Ti_{20}O_{39}$ amounts to 5.294 eV. Then the cohesive energy of the ideal $Ti_{20}O_{39}$ structure is found to be -2375.3 eV per $Ti_{20}O_{39}$ "molecule". The cohesive energy translated into per TiO_x is then as follows, -124.3 eV for TiO_2, -118.8 eV for $TiO_{1.95}$ and -97.6 eV for $TiO_{1.75}$. This feature shows that the cohesive energy tends to increase as x in TiO_x decreases. As is well known [1, 2], $TiO_{1.95}$ contains $\{1\,3\,2\}$ CS planes and $TiO_{1.75}$, well-ordered arrays of $\{1\,2\,1\}$ CS planes. As x in TiO_x decreases, the concentration of CS planes increases, which results in an increase in the free energy. Therefore, the increase in the cohesive energy must be ascribed to the increase in the concentration of CS planes.

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