Electron-density distribution in ilmenite-type crystals III. Nickel (II) titanium (IV) trioxide, NiTiO_3

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Abstract

The electron-density distribution in a crystal of NiTiO_3 has been investigated by means of the single crystal X-ray diffraction method. A small amount of partial disorder was observed in the cation arrangement of the examined crystal. The difference electron-density maps showed an aspherical distribution of $3d$ electrons of the Ni^{2+} ion in the octahedral crystal field. Electron populations of the a , $e(t_{2g})$ and $e(e_g)$ orbitals of Ni^{2+} were refined on the basis of the $3(C_3)$ crystal field, employing aspherical scattering factors for the cation. The refinement gave the populations 1.84(9), 4.00(10) and 2.16(7) for the respective orbitals. The Ti^{4+} ion lies in a negative region of the difference Fourier map after the spherical atom refinement, and a positive peak exists on the threefold axis at a position 0.49 Å apart from the Ti^{4+} ion towards the Ni^{2+} ion. These residual densities around Ti^{4+} are supposed to be caused by positive charge of the neighbouring Ni^{2+} ion. A residual peak is also observed at the middle of the neighbouring Ni^{2+} and Ti^{4+} along the threefold axis, which might be an indication of a metal-metal bonding. Refinements with anharmonic thermal parameters for the cations, up to the fourth order, revealed that anharmonicity is small at the room temperature in the present crystal.

Introduction

Ilmenite-type crystals have the same atomic arrangement as that in the corundum structure, but they contain two kinds of metal atoms with an ordered state. Electron-density distributions in corundum-type crystals, Ti_2O_3 and V_2O_3 , were reported by Vincent, Yvon, Grüttner & Ashkenaji (1980) and Vincent, Yvon & Ashkenaji (1980). They observed deformation densities of d electrons suggesting metal-metal interactions. Kidoh, Tanaka, Marumo & Takei (1984a,b) reported the electron-density distributions in ilmenite-type crystals, CoTiO_3 and MnTiO_3 , finding aspherical distributions of d electrons around the Co^{2+} and Mn^{2+} ions and strongly deformed electron clouds around Ti^{4+} ions. The degree of deformation was different in these two crystals. On the other hand, they could not find clear indication of

metal-metal bonding. Therefore, it is of interest to investigate systematically electron-density distributions in a series of ilmenite-type crystals to examine the relation between structural details and deformation of electron clouds. This paper reports the results of a study on electron-density distribution in a crystal of NiTiO_3 carried out with the single-crystal X-ray diffraction method.

Experimental

The ilmenite-type crystal NiTiO_3 used in this study was synthesized by Takei, Hosoya and Kojima (1982). The starting materials were reagent grade $\text{Ni}(\text{COO})_2 \cdot n\text{H}_2\text{O}$ and reagent grade TiO_2 . An equimolar mixture of these reagents was heated for 4 h at 1000°C in a flow of $\text{CO}_2\text{-N}_2$ gas, and then pressed into a rod approximately 8 mm in diameter and 80 mm in length. Nutrient rods of NiTiO_3 were prepared from this pressed rod by sintering for 2 h at 1100°C under the same atmosphere. Crystal growth was performed by the floating-zone method in a lamp image infrared-heating furnace with a tungsten-iodine lamp under the condition of 1400°C molten zone temperature and 3mm/h growth rate in $\text{CO}_2\text{-N}_2$ atmosphere.

A piece of the crystal obtained was shaped into a sphere of 0.146 mm in diameter by the Bond's method (Bond, 1951). The specimen was confirmed to have an ilmenite-type structure by taking Weissenberg photographs, and then mounted on a Rigaku automated four-circle diffractometer (AFC-5UD).

The cell parameters were determined from 2θ values of 75 reflections higher than 60° , measured on the four-circle diffractometer with $\text{MoK}\alpha_1$ radiation ($0.70926 \text{ \AA}$). The crystal data are given in Table 1. Intensity measurements were performed with graphite-monochromated $\text{MoK}\alpha$ radiation ($0.71069 \text{ \AA}$) in a sextant of the reciprocal space lower than 145° in 2θ . In addition a total of 98 strong reflections were measured in the full reciprocal space for anisotropic extinction corrections.

TABLE 1. Crystal data of NiTiO_3 .

space group	$R\bar{3}$
a(Å)	5.0394(9)
c(Å)	13.811(3)
Z	6
D_x (g cm^{-3})	5.070
μ for $\text{MoK}\alpha$ (cm^{-1})	129.8*

* Calculated from the mass attenuation coefficients given in International Tables for X-Ray Crystallography (1974).

TABLE 2. Experimental conditions.

Diameter of specimen (mm)	0.146
Radiation	MoK_α
Monochromator	Graphite
Max of 2θ ($^\circ$)	145
Scan technique	$\omega - 2\theta$
Scan speed	2° min^{-1} in 2θ
Number of measured reflections	1750
Number of used reflections	1460
Number of independent reflections	1235
Reflections for anisotropic extinction corrections	98

Measurement was repeated up to 10 times, when $\sigma(|F_o|)/|F_o|$ was larger than 0.005. The reflections with $|F_o| < 3\sigma(|F_o|)$ were deleted from the data set used in the subsequent calculations. A number of reflections and other experimental conditions are given in Table 2.

Intensities were corrected for Lp factors. Absorption corrections were carried out utilizing the values of the absorption correction factors A^* for spherical crystals given in *International Tables for X-Ray Crystallography* (1967). The values of A^* are in the range 3.84~2.88. The mean path length, $T=(dA^*/d\mu)/A^*$, was calculated for each reflection for the purpose of secondary extinction correction, where μ is the linear absorption coefficient.

Refinement

In this study three kinds of refinements were carried out. The first is the usual structure refinement with spherical scattering factors, the second a refinement with aspherical scattering factors, and the third subsequently performed refinement with anharmonic thermal parameters. In the refinements with aspherical scattering factors, electron populations on the respective $3d$ orbitals of Ni^{2+} ions were included into the parameters to be refined. Atomic scattering factors for Ni^{2+} and Ti^{4+} ions and dispersion-correction factors were taken from *International Tables for X-Ray Crystallography* (1974). For the O^{2-} ion, the scattering factor given by Tokonami (1965) was used.

a) Refinement with spherical scattering factors

At the initial stage of refinement, an ideal ilmenite structure was assumed. The refinement was carried out with a modified version of the full-matrix least-squares program LINKT, which includes the extinction corrections after Becker and Coppens (1974a,b, 1975) and a subroutine to refine anharmonic thermal parameters after the method of Tanaka and Marumo (1983). Since a least-squares calculation on the assumption of the type II extinction effects with a Gaussian mosaic-spread distribution gave smaller R and Rw values (0.0207 and 0.0253) than those with the type I extinction corrections (0.0213 and 0.0260), the subsequent refinements were performed with the former model for the extinction corrections. At the second stage the partial disorder of the cations was taken into consideration. The chemical formula was assumed as $(\text{Ni}_q\text{Ti}_r)(\text{Ti}_u\text{Ni}_v)\text{O}_{q+v+2(r+u)}$, and the population parameters were refined with normalization of the larger values between $q+r$ and $u+v$ to unity. The calculation converged to give the values 0.96(1), 0.04(1), 0.95(1) and 0.04(1) for q , r , u and v , respectively. These values give the composition of $(\text{Ni}_{0.96}\text{Ti}_{0.04})(\text{Ti}_{0.95}\text{Ni}_{0.04}\square_{0.01})\text{O}_3$ for the present crystal. The final R and Rw values with this refinement were 0.0192 and 0.0211, respectively. A section of the difference Fourier map calculated at this stage is shown in Fig. 1.

b) Refinement with aspherical scattering factors

Since indication of an aspherical distribution was observed in Fig. 1 around the Ni^{2+} ion, refinements were continued by adopting aspherical scattering factors for Ni^{2+} ions on the assumptions of the $m\bar{3}m$ (O_h), $\bar{3}m$ (D_{3d}) and $3(C_3)$ site symmetries to it. The t_{2g} orbitals split into a_g and $e_g(t_{2g})$ orbitals in the $\bar{3}m$ (D_{3d}) crystal field. When the quantization axis z is chosen along the threefold axis and x in the plane determined by z and one of the Ni-O bonds, the wave functions for the respective $3d$ orbitals of $m\bar{3}m$ (O_h) symmetry are rewritten as follows.

$$\begin{aligned}
 a_g &: \psi_{320} \\
 e_g(t_{2g}) &: \begin{cases} \sqrt{\frac{2}{3}}\psi_{322} + \sqrt{\frac{1}{3}}\psi_{32-1} \\ \sqrt{\frac{2}{3}}\psi_{32-2} - \sqrt{\frac{1}{3}}\psi_{321} \end{cases} \\
 e_g(e_g) &: \begin{cases} \sqrt{\frac{1}{3}}\psi_{322} - \sqrt{\frac{2}{3}}\psi_{32-1} \\ \sqrt{\frac{1}{3}}\psi_{32-2} + \sqrt{\frac{2}{3}}\psi_{321} \end{cases}
 \end{aligned}$$

Here, the a_g and $e_g(t_{2g})$ orbitals are degenerated in the $m\bar{3}m$ (O_h) crystal field. When

the ratio of the electron population of a_g to that of $e_g(t_{2g})$ changes from the value 1/2 for the $m\bar{3}m$ (O_h) field, the symmetry of electron distribution lowers to $\bar{3}m$ (D_{3d}).

The scattering factors for an electron in these orbitals have the following forms,

$$\begin{aligned}
 f\{a_g\} &= \langle j_0 \rangle - \frac{5}{7} (3 \cos^2 \theta - 1) \langle j_2 \rangle \\
 &\quad + \frac{9}{28} (35 \cos^4 \theta - 30 \cos^2 \theta + 3) \langle j_4 \rangle, \\
 f\{e_g(t_{2g})\} &= \langle j_0 \rangle + \frac{5}{14} (3 \cos^2 \theta - 1) \langle j_2 \rangle \\
 &\quad - \frac{1}{28} (35 \cos^4 \theta - 30 \cos^2 \theta + 3) \langle j_4 \rangle \\
 &\quad + \frac{5}{\sqrt{2}} \sin^3 \theta \cos \theta \cos 3\varphi \langle j_4 \rangle, \\
 f\{e_g(e_g)\} &= \langle j_0 \rangle - \frac{1}{8} (35 \cos^4 \theta - 30 \cos^2 \theta + 3) \langle j_4 \rangle \\
 &\quad - \frac{5}{\sqrt{2}} \sin^3 \theta \cos \theta \cos 3\varphi \langle j_4 \rangle.
 \end{aligned}$$

where values of $\langle j_n \rangle$ are given in *International Tables for X-Ray Crystallography* (1974), and θ and φ are the angular coordinates of scattering vector (Weiss & Freeman, 1959; Iwata, 1977).

At first, electron populations were refined on the $m\bar{3}m$ (O_h) symmetry together with other parameters by fixing the total number of $3d$ electrons of Ni^{2+} to eight and the number of electrons on the $e_g(t_{2g})$ orbital to twice of the number of electrons on a_g . Then the R and R_w values reduced to 0.0181 and 0.0207, respectively. The values of 1.86(5) and 2.42(5) were obtained for the populations of a_g and $e_g(e_g)$ orbitals, respectively. A section of the difference Fourier map calculated at this stage is shown in Fig. 2. Then, the refinement was continued on the assumption of the $\bar{3}m$ (D_{3d}) site symmetry for Ni^{2+} , and the R and R_w values were reduced to 0.0177 and 0.0202, respectively.

Finally, a refinement was tried by assuming the $3(C_3)$ crystal field for Ni^{2+} , which is the real site symmetry of the ion. Under the $3(C_3)$ symmetry, the coefficients of ϕ_{322} and ϕ_{32-1} can be changed more widely than the values for the $\bar{3}m(D_{3d})$ symmetry in the expressions of $e(t_{2g})$ and $e(e_g)$ wave functions. For the estimation of the coefficient calculations were performed by placing ten point-charges around the Ni^{2+} ion: six $2e$ at the surrounding O^{2-} sites, three $-2e$ at the nearest Ni^{2+} ion sites

and one $-4e$ at the nearest Ti^{4+} ion site on the z axis. By calculating the Hermite matrix elements of the secular equation, the energy eigenvalues were obtained as follows,

$$\varepsilon_1 = 7.177 (e(e_g) \text{ orbital})$$

$$\varepsilon_2 = -4.270 (e(t_{2g}) \text{ orbital})$$

$$\varepsilon_3 = -5.815 (a \text{ orbital}).$$

The a orbital have the lowest energy according to this simple estimation, but difference from the value for $e(t_{2g})$ is not so large. The wave functions of the respective orbitals are calculated by substituting the values of respective energy eigenvalues in the Hermite matrix, and can be written in the following forms by normalizing.

$$\begin{aligned} a : & \quad \phi_{320} \\ e(t_{2g}) : & \quad \begin{cases} 0.8249\phi_{322} + (0.5638 - 0.04104i)\phi_{32-1} \\ 0.8249\phi_{32-2} - (0.5638 + 0.04104i)\phi_{321} \end{cases} \\ e(e_g) : & \quad \begin{cases} 0.5653\phi_{322} - (0.8228 - 0.05858i)\phi_{32-1} \\ 0.5653\phi_{32-2} + (0.8228 + 0.05858i)\phi_{321} \end{cases} \end{aligned}$$

The scattering factors per one electron for the respective orbitals are,

$$\begin{aligned} f\{a\} = & \langle j_0 \rangle - \frac{5}{7} (3 \cos^2 \theta - 1) \langle j_z \rangle \\ & + \frac{9}{28} (35 \cos^4 \theta - 30 \cos^2 \theta + 3) \langle j_4 \rangle, \\ f\{e(t_{2g})\} = & \langle j_0 \rangle + 0.3720 (3 \cos^2 \theta - 1) \langle j_z \rangle \\ & - 0.0320 (35 \cos^4 \theta - 30 \cos^2 \theta + 3) \langle j_4 \rangle \\ & + (3.4883 \cos 3\varphi - 0.2483 \sin 3\varphi) \sin^3 \theta \cos \theta \langle j_4 \rangle, \\ f\{e(e_g)\} = & \langle j_0 \rangle - 0.0148 (3 \cos^2 \theta - 1) \langle j_z \rangle \\ & - 0.1287 (35 \cos^4 \theta - 30 \cos^2 \theta + 3) \langle j_4 \rangle \\ & - (3.4883 \cos 3\varphi - 0.2483 \sin 3\varphi) \sin^3 \theta \cos \theta \langle j_4 \rangle. \end{aligned}$$

The obtained wave functions and scattering factors are close to those for the $m\bar{3}m(O_h)$ symmetry.

The populations obtained with these scattering factors are 1.84(9), 4.00(10) and

2.16(7) for a , $e(t_{2g})$ and $e(e_g)$ orbitals, respectively. The R and Rw factors are 0.0176 and 0.0201. A section of the difference Fourier map calculated after this refinement is shown in Fig. 3.

c) Refinement with anharmonic thermal parameters

Since anharmonic thermal vibrations were recognized in a crystal of MnTiO₃ (Kidoh, et. al., 1984), refinement was tried by taking into account anharmonic thermal vibrations for the cations with the generalized Willis' method (Willis, 1969; Tanaka & Marumo, 1984). The symmetries of the Ni²⁺ and Ti⁴⁺ sites are 3(C₃) in NiTiO₃. Therefore, the potentials are expressed in the following form, when the higher order terms than fourth are neglected;

$$\begin{aligned}
 V(u) = & V_0 + \frac{1}{2} [b_1(u_1^2 + u_2^2) + b_3 u_3^2] \\
 & + c_{111}(u_1^3 - 3u_1 u_2^2) + c_{222}(u_2^3 - 3u_2 u_1^2) \\
 & + c_{333} u_3^3 + c_{311}(u_1^2 u_3 - u_2^2 u_3) \\
 & + q_{1111}(u_1^4 + u_1^2 u_2^2 + u_2^4) + q_{3333} u_3^4 \\
 & + q_{1133}(u_1^2 u_3^2 + u_2^2 u_3^2) \\
 & + q_{1131}(u_1^3 u_3 - 3u_1 u_2^2 u_3) \\
 & + q_{2233}(u_2^3 u_3 - 3u_2^2 u_1 u_3),
 \end{aligned}$$

where u_1 , u_2 and u_3 are the components of the displacement vector along rectangular coordinates defined for each cation as follows; the u_3 axis lies along the threefold axis and u_1 in the plane determined by u_3 and the Ni-O bond which is nearest to the (01 $\bar{1}$ 0) plane.

The refinement was carried out by changing the anharmonic parameters c_{ijk} and q_{ijkl} together with all other parameters. The least-squares calculations gave R and Rw factors of 0.0172 and 0.0199, respectively. The final positional and anisotropic thermal parameters are tabulated in Table 3, and the harmonic and anharmonic potential parameters are listed in Table 4.

Discussion

The interatomic distances in the NiO₆ and TiO₆ octahedra are shown in Fig. 4. In accordance with the larger ionic radius, the Ni²⁺ ion has a larger mean bond length with surrounding O²⁻ ions (2.080 Å) than that for Ti⁴⁺ ion (1.983 Å). The O-Oⁱⁱ edge on the shared face is the shortest among the O-O edges in the NiO₆ octahedron,

TABLE 3. Final parameters for $(\text{Ni}_{0.96}\text{Ti}_{0.04})(\text{Ti}_{0.95}\text{Ni}_{0.04}\square_{0.01})\text{O}_3$.Positional and thermal parameters ($\text{\AA}^2$)

Ni	z	0.35063(1)	O	x	0.31490(11)
	U_{11}	0.00450(3)		y	0.01602(11)
	U_{33}	0.00516(4)		z	0.24661(3)
Ti				U_{11}	0.00487(12)
	z	0.14421(1)		U_{22}	0.00566(12)
	U_{11}	0.00440(4)		U_{33}	0.00639(11)
	U_{33}	0.00465(5)		U_{12}	0.00258(10)
				U_{13}	0.00036(9)
				U_{23}	0.00119(9)

Extinction parameters (10^{-4}cm)

G_{11}	223(31)	Electron populations	
G_{22}	52(6)		
G_{33}	32(3)		a
G_{12}	34(12)		$e(t_{2g})$
G_{13}	-34(8)		$e(e_g)$
G_{23}	-24(4)		

The form of the anisotropic temperature factor is defined as

$$\exp\{-2\pi^2[(h^2+k^2)a^2U_{11}+l^2c^2U_{33}+\frac{1}{2}hka^2U_{11}]\}$$

whereas the shared edge O-O^{vi} is the shortest in the TiO_6 octahedron as in CoTiO_3 and MnTiO_3 (Kidoh et al., 1984a, b). The Ni^{2+} and Ti^{4+} ions are largely shifted towards the vacant octahedral sites from the centers of the respective coordination octahedra as in other ilmenite- and corundum-type crystals. In the NiO_6 octahedron, the distance between the Ni^{2+} ion and the shared face is 1.4365 Å and that between

TABLE 4. Harmonic ($10^{-19} \text{J}\text{\AA}^{-2}$), third anharmonic ($10^{-19} \text{J}\text{\AA}^{-3}$) and fourth anharmonic ($10^{-19} \text{J}\text{\AA}^{-4}$) potential parameters at 306 K, with e.s.d.'s in parentheses. Thermal parameter values are taken $U_{11}=kT/b_1$, $U_{33}=kT/b_3$, k : Boltzman constant, T : temperature (K).

	Ni	Ti
b_1	9.39(9)	9.61(10)
b_3	8.19(6)	9.08(9)
c_{111}	-0.8(5)	1.1(7)
c_{222}	0.4(5)	0.1(6)
c_{311}	0.2(7)	-1.2(11)
c_{333}	-0.04(50)	-0.4(6)
q_{1111}	7.1(30)	10.0(48)
q_{1133}	-49.5(235)	-70.5(369)
q_{3333}	15.1(71)	20.1(120)
q_{1131}	18.3(218)	-51.7(320)
q_{2223}	-12.8(211)	-39.1(304)

Ni^{2+} and the opposite face $0.9590\text{\AA}$. In the TiO_6 octahedron, the corresponding distances are $1.4144\text{\AA}$ and $0.7939\text{\AA}$, respectively. Thus, the ratio of the distance from the shared face to that from the opposite face is much larger in the TiO_6 octahedron (1.782) than in NiO_6 (1.498). Effect of the cation shifts also appears on the cation-oxygen bond distances as seen in Fig. 4.

In the difference Fourier map after the refinement with spherical scattering factors (Fig. 1), there are six negative and eight positive peaks around the Ni site. The negative peaks are on the Ni-O bonds at distances of $0.42\text{\AA}$ from the Ni site on the side of the shared face and at $0.46\text{\AA}$ on the other side. The depth of the peaks are $-1.58\text{e}\text{\AA}^{-3}$ and $-1.33\text{e}\text{\AA}^{-3}$, respectively. One of the positive peaks lies on the threefold axis at $0.41\text{\AA}$ from Ni^{2+} on the side of the shared face, having the height $0.41\text{e}\text{\AA}^{-3}$. On the opposite side of the Ni^{2+} ion, there is a peak with the height

FIG. 1. The section of the difference Fourier map on the plane containing the Ni^{2+} , Ti^{4+} and O^{2-} ions after the refinement with spherical scattering factors. The filled and open circles indicate the Ni^{2+} and Ti^{4+} sites. The O^{2-} site is denoted with a cross. Contours are at intervals of $0.20\text{e}\text{\AA}^{-3}$. Negative and zero contours are in broken and dashed-dotted lines, respectively. Bond lengths are given in the $\text{\AA}$ unit.

FIG. 2. The section of the difference Fourier map after the refinement with aspherical scattering factors assuming the $m3m(\text{O}_h)$ crystal field, on the plane containing the Ni^{2+} , Ti^{4+} and O^{2-} ions.

$0.48\text{e}\text{\AA}^{-3}$ at $0.80\text{\AA}$ from Ni^{2+} . The remaining six positive peaks lie also on the quasi threefold axes of the coordination octahedron, avoiding the Ni-O bonds at distances of $0.51\text{\AA}$ from Ni^{2+} on the side of the shared face and $0.43\text{\AA}$ on the other side with the heights of $0.81\text{e}\text{\AA}^{-3}$ and $0.96\text{e}\text{\AA}^{-3}$, respectively. These negative and positive peaks are supposed to be due to the aspherical distribution of $3d$ electrons of the Ni^{2+} ion in the quasi-octahedral field. In ordinary refinements, the number of electrons is considered to be $8/5$ per unit orbital for the respective $3d$ orbitals of Ni^{2+} . The refinement with aspherical scattering factors assuming the $m3m(\text{O}_h)$ crystal field greatly diminished these residual densities around Ni^{2+} ion, as seen in Fig. 2. When the

FIG. 3. The section of the difference Fourier map after the refinement with aspherical scattering factors assuming the $3(C_3)$ crystal field, on the plane containing the Ni^{2+} , Ti^{4+} and O^{2-} ions.

FIG. 4. Bond lengths(Å) in the NiO_6 octahedron and TiO_6 octahedron. Symmetry code: *none* x, y, z ; (i) $-y, x-y, z$;

$$(ii) y-x, -x, z; (iii) \frac{1}{3}-x, \frac{2}{3}-y, \frac{2}{3}-z;$$

$$(iv) \frac{1}{3}+y, \frac{2}{3}-x+y, \frac{2}{3}-z; (v) \frac{1}{3}+x-y,$$

$$\frac{2}{3}+x, \frac{2}{3}-z; (vi) \frac{2}{3}-x, \frac{1}{3}-y, \frac{1}{3}-z;$$

$$(vii) \frac{2}{3}+y, \frac{1}{3}-x+y, \frac{1}{3}-z; (viii) \frac{2}{3}+x-y,$$

$$\frac{1}{3}+x, \frac{1}{3}-z.$$

assumed site symmetry was lowered to $\bar{3}m(D_{3d})$, a small reduction of the residual densities was observed around Ni^{2+} . However, no significant difference was observed between the difference Fourier maps after the refinements with $\bar{3}m(D_{3d})$ and that with $3(C_3)$.

For the Ti^{4+} ion, on the other hand, there are six positive peaks on the Ti-O bonds at 0.43 Å from the Ti site on the side of shared face with the height $1.30e\text{Å}^{-3}$ and at 0.48 Å on the other side with the height $0.73e\text{Å}^{-3}$ after the ordinary refinement. In addition, there is a positive peak with the height $1.42e\text{Å}^{-3}$ on the

threefold axis at 0.49 Å from Ti^{4+} on the side of the shared face. The peak on the threefold axis forms a large positive region together with those on the Ti-O bonds lying on the side of the shared face. The positive and negative peaks around Ti^{4+} suggest that the electron cloud of Ti^{4+} is deformed to relieve the metal-metal repulsion. A similar deformation of electron clouds is observed around the Ti^{4+} ion in CoTiO_3 .

At the middle point between Ni^{2+} and Ti^{4+} ions on the threefold axis, a large positive peak ($1.08\text{e}\text{\AA}^{-3}$) exists in Fig. 3 in contrast to the cases of MnTiO_3 and CoTiO_3 (Kidoh *et al.*, 1984a, b). Vincent *et al.* (1980) has reported existence of a metal-metal σ bonding across the shared face of the TiO_6 octahedra in Ti_2O_3 . The peak might be an indication of a metal-metal bonding between Ni^{2+} and Ti^{4+} ion.

According to the energy levels estimated on the simple model with the $3(\text{C}_3)$ symmetry, electron populations on the a , $e(t_{2g})$ and $e(e_g)$ orbitals are 2, 4 and 2, respectively, in the ground state. The obtained values 1.84(9), 4.00(10) and 2.16(7) for the respective orbitals are close to the expected values. However, if these values are correct, the order of the energy levels of the a and $e(t_{2g})$ orbitals should be reversed. A similar situation resulted also in CoTiO_3 Kidoh, *et al.*, 1984).

Although a refinement was carried out by employing anharmonic thermal parameters for the cations, the effect of anharmonic thermal vibration was revealed to be small in the present case.

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