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The Compound Cr_2TiO_5 in the System Cr_2O_3–TiO_2

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The compound Cr_2TiO_5 could be synthesized as a stoichiometric single phase above 1660°C in air. Application of selected area electron diffraction, high resolution electron microscopy and powder X-ray diffraction studies showed that Cr_2TiO_5 is isomorphous with $CrFeTiO_5$, with V_3O_5 type structure. It is monoclinic, $a = 7.020(1)$ Å, $b = 5.025(1)$ Å, $c = 9.945(2)$ Å and $\beta = 111.43(2)°$. It was found that Cr_2TiO_5 is unstable relative to a mixture of Cr_2O_3 (*ss*) and a so-called "*E*" phase, below 1660°C.

Introduction

Higher members of the homologous series $Cr_2Ti_{n-2}O_{2n-1}$, with $n = 6, 7, 8$ and 9 have been characterized by the X-ray diffraction technique (*1–4*). These members may be formally derived by the application of crystallographic shear (CS) to the basic rutile structure (*5*). Recent work with an electron microscope revealed that the $n = 9$ member of the $(121)_r$CS family did not exist but belonged to a high index CS family instead of $(121)_r$CS (*6*). Moreover, there existed "a continuous ordered solid solution" in the range of $n > 8$ where the CS planes were reoriented cooperatively pivoting around the $[1\bar{1}1]_r$ zone axis. Even though the compounds with $n \geq 6$ in the series of $Cr_2Ti_{n-2}O_{2n-1}$ have been intensively investigated, the stabilities and the structural analysis of the lower homologues, i.e. with $n \leq 5$ in the series still remain to be solved. One of the members, $Cr_2Ti_2O_7$ ($n = 4$), was first characterized by X-ray diffraction to be isomorphous with $CrFeTi_2O_7$ whose structure was determined using single crystal X-ray diffraction (*7*).

A very small amount of Cr_2TiO_5, the second member of the lower series, was first prepared by melting a sample with the stoichiometric composition by Åsbrink, Friberg, Magnéli, and Andersson (*8*). However, the arc melting method was unsuitable for the determination of the stability field of the compound. Kwestroo and Roos followed their work and reported that the V_3O_5 type phase was not formed as a pure phase but could be stabilized by addition of Fe, as in the Cr_2O_3–TiO_2 system (*9*). Grey and Reid also reported V_3O_5 type phases in the series of $(Cr_{1-x}Fe_x)_2TiO_5$, $x = 0.50$ and 0.85, (*10*).

The stability and the details for the preparation of pure Cr_2TiO_5 have not been reported. Recently, the authors found the existence of the Cr_2TiO_5 compound as a single phase in the study of the phase relations of the Cr_2O_3–TiO_2 system (*11*).

The present work was carried out in order to examine the stable region in air and the structure of the Cr_2TiO_5 compound.

Experimental

A mixture of Cr_2O_3 and TiO_2 powders with desired composition was pelleted,

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embedded in a powder mixture of the same composition and then heat treated in air. The specimen obtained from the central part of the quenched pellet specimen was used for the phase analysis. Another heat-treatment method was also employed by sealing a pelletized sample in a capsule of platinum–20% rhodium. Both preparations gave the same results for the phase analysis. It was concluded, therefore, that the composition change at the central part of the pellet due to volatilization of chromia itself could be within an experimental error of 1 wt% of the composition.

X-ray powder diffraction patterns were obtained using Cu*Kα* radiation through an X-ray diffractometer (Rigaku-2078) with a graphite monochromator. Pure Si and SiO_2 (α-quartz) were used as internal standards. The determination of the lattice parameters and the indexing of the powder pattern were carried out by the least square refinement method with an electronic computer.

Selected area electron diffraction patterns of the compound were obtained using a H-TEM 700 (Hitachi Co., Ltd.) electron microscope equipped with a goniometer stage. High resolution electron micrographs were taken after tilting the thin fragment with magnification up to ×400,000 using a JEM-100CX (JEOL Co., Ltd.) equipped with a high resolution goniometer stage. Samples for the electron microscopic examination were prepared by crushing the coarse grain at the central part of the heat-treated specimen under *n*-butanol in an agate mortar. The resultant suspension was mounted on a carbon-coated holey support film (*12*). Only thin fragments lying over holes in the film were tilted until an incident beam was parallel to the desired zone axis.

Results

1. Stability of Cr_2TiO_5

A part of the phase diagram for the system Cr_2O_3–TiO_2 determined by the authors is shown in Fig. 1. The Cr_2TiO_5 compound existed as a single phase when a sample of 34.46 wt% $TiO_2 \cdot 65.54$ wt% Cr_2O_3 (stoichiometric composition of Cr_2TiO_5) was heated at 1680°C for 48 hr. The shift of the starting composition by 1 wt% Cr_2O_3 from the stoichiometry resulted in coexistence of a

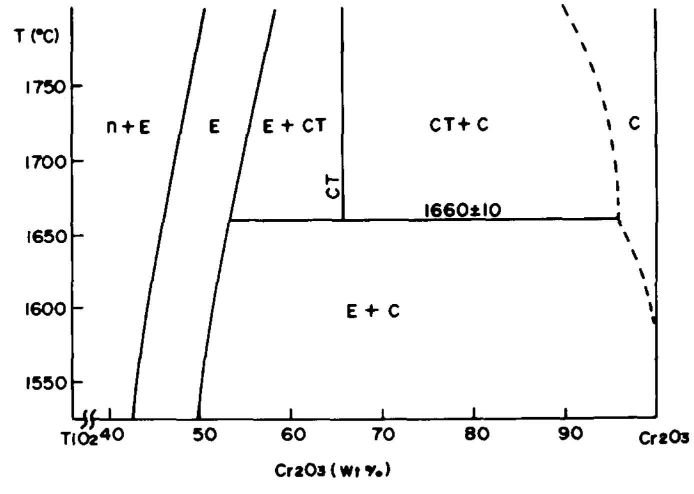

FIG. 1. A part of the phase diagram of the system Cr_2O_3–TiO_2. *C*; Cr_2O_3(*ss*), *CT*; Cr_2TiO_5, *E*; *E* phase, *n*; high temperature phase.

small amount of the *E* phase or Cr_2O_3 (*ss*) with Cr_2TiO_5 according to the composition. The long time treatment for 7 days at the higher temperature of 1765°C gave the same results, which suggested that Cr_2TiO_5 has no solid solubility and exists as a stoichiometric compound within experimental error.

On the contrary, when the sample of 65.54 wt% Cr_2O_3 was heat treated at 1650°C for 24 hr, the phase was composed of Cr_2O_3 (*ss*) and the *E* phase. Heating for 48 hr at this temperature gave the same result. Thus the past failure of preparations of Cr_2TiO_5 cannot be attributed to the kinetics of the reaction but to the necessity to use higher temperatures than 1660°C. Cr_2TiO_5 formed above 1660°C was then reheated in a sealed capsule at 1640°C. The Cr_2TiO_5 compound was found to decompose to Cr_2O_3 (*ss*) and the *E* phase, depending on the heat-treatment time. Cr_2TiO_5, Cr_2O_3 (*ss*), and the *E* phase were found even after the heating for 2 hr but Cr_2TiO_5 was completely decomposed after 12 hr at the same temperature. The stabilization temperature for Cr_2TiO_5 was, therefore, determined to be 1660 ± 10°C in the present work.

2. Characterization of the Structure of Cr_2TiO_5

The X-ray powder pattern of Cr_2TiO_5 was very similar to that of $CrFeTiO_5$ isomorphous with V_3O_5 structural type. The indexing of the pattern of Cr_2TiO_5 was, therefore, made on the basis of the data on $CrFeTiO_5$ characterized by Grey *et al.* (*10*) and the lattice parameters of Cr_2TiO_5 were determined to be $a = 7.020(1)$ Å, $b = 5.025(1)$ Å, $c = 9.945(2)$ Å, and $\beta = 111.43(2)°$. The lattice parameters were refined by the least square method. The data are given in Table I. The lattice parameters of Cr_2TiO_5 are similar to those of $CrFeTiO_5$ which were reported to be $a = 7.001$ Å, $b = 5.001$ Å, $c = 10.058$ Å, and $\beta = 111.07°$ (*10*). It is concluded that the compound Cr_2TiO_5 is not pseudobrookite type but isomorphous with the V_3O_5 structural type.

TABLE I

X-RAY POWDER DATA FOR Cr_2TiO_5

hkl	2θ (Obsd.)	2θ (Calcd.)	*I*
0 0 2	19.16	19.17	w
0 1 1	20.16	20.11	vvw
−2 0 2	27.04	27.03	vst
2 0 0	27.28	27.29	vvw
−2 1 1	31.10	31.07	vst
0 1 3	34.08	34.09	vst
0 2 0	35.84	35.74	m
−2 1 3	36.58	36.57	vvw
2 1 1	36.95	36.96	st
−2 0 4	38.60	38.57	vvw
0 0 4	38.91	38.91	vvw
−1 2 2	40.82	40.79	w
0 2 2	40.93	40.86	m
−3 1 1	43.03	42.98	w
2 2 0	45.51	45.54	w
0 1 5	52.69	52.68	st
−3 2 2	53.70	53.69	vst
4 0 0	56.32	56.29	vst

$a = 7.020(1)$ Å, $b = 5.025(1)$ Å, $c = 9.945(2)$ Å, $\beta = 111.43(2)°$

The characterization of the structure of Cr_2TiO_5 was confirmed by the electron diffraction technique. Electron diffraction patterns were obtained along several zone axes by tilting the thin fragments, so that the zone axis was parallel to an incident beam. The reciprocal section of each pattern was determined on the basis of the X-ray diffraction data. All the electron diffraction patterns gave sharp spots without any diffuseness, as shown in Fig. 2. The electron diffraction patterns shown in Figs. 2a, b were obtained from [100] and [010] zone axes, respectively, and the indexing of the spots was compatible with the data by X-ray diffraction methods.

The high resolution electron micrograph of the lattice image of Cr_2TiO_5 is shown in Fig. 3, which was viewed down along the *a*-axis and is in good agreement with the

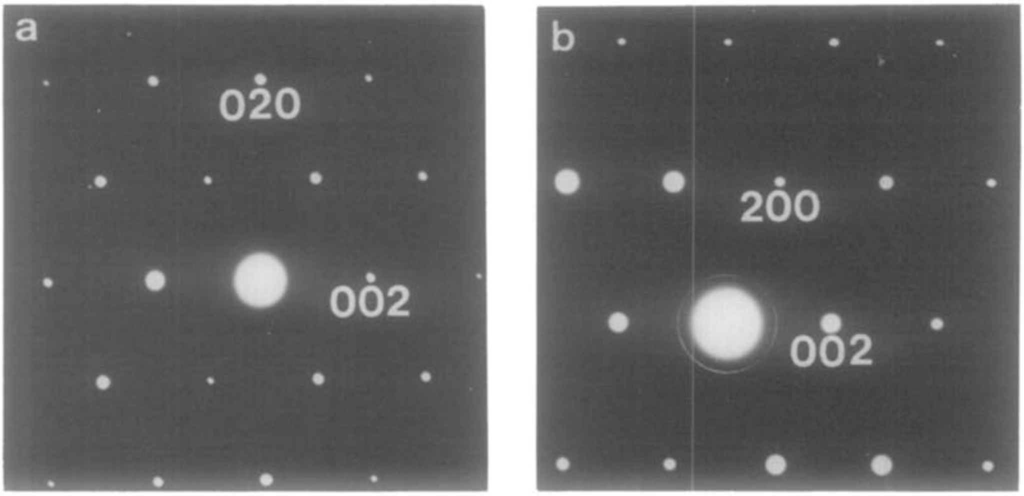

FIG. 2. Electron diffraction patterns obtained on the fragments of Cr_2TiO_5, (a) pattern on [100] zone axis and (b) pattern on [010] zone axis.

idealized structural model for Cr_2TiO_5 discussed below.

Discussion

In the present study, the lowest end member with $n = 3$, Cr_2TiO_5, in the series of $Cr_2Ti_{n-2}O_{2n-1}$ was found to be stable above 1660 ± 10°C. Cr_2TiO_5 had no solid solubility and was regarded as a pure stoichiometric compound. It was also confirmed that Cr_2TiO_5 decomposed to Cr_2O_3 (*ss*) and the *E* phase at the temperature lower than 1660°C. Thus, due to the lack of data on thermodynamic stability of this compound, it was considered that the past researchers on this system could not prepare the pure Cr_2TiO_5 by the reaction of Cr_2O_3 with TiO_2 below 1660°C.

The structure of Cr_2TiO_5 was characterized by X-ray and electron diffraction methods in the present study. Cr_2TiO_5 was found to be isomorphous with the V_3O_5 type structure (*13*) which could be derived from the application of the crystallographic shear of $\frac{1}{2}[0\bar{1}1]_r(121)_r$ to the basic rutile structure. However, an alternative representation based on the α-PbO_2 structure (*14*) isomorphous with the high pressure form of rutile (*15*) is also possible. An idealized model for the structure of Cr_2TiO_5 is shown in Fig. 4 using the representation developed by Andersson and Galy (*16*). In the case that the structure is projected along the *b*-axis with 5 Å separation common to V_3O_5 and α-PbO_2 type structure, oxygen atoms can be seen to produce pseudohexagonal layers with the metal atoms occupying octahedral sites which give a rather complex arrangement of octahedra mutually sharing corners, edges, and faces. The unit cell axes of Cr_2TiO_5 are related to those for α-PbO_2 structural type by following vectorial expressions,

$$a = -a_{\alpha\text{-PbO}_2} + b_{\alpha\text{-PbO}_2}$$

$$b = c_{\alpha\text{-PbO}_2}$$

$$c = 2a_{\alpha\text{-PbO}_2} + \tfrac{1}{2}b_{\alpha\text{-PbO}_2}.$$

Recently, more suitable unit cells with the *c*-axis parallel to $b_{\alpha\text{-PbO}_2}$ were chosen for the interpretation of the ordered intergrowth phases between α-PbO_2 and V_3O_5 type cell in the complex series of $(Cr, Fe)_{2p}(Ti, Zr)_{p+2q}O_{5p+4q}$ (*17*). Alternative new

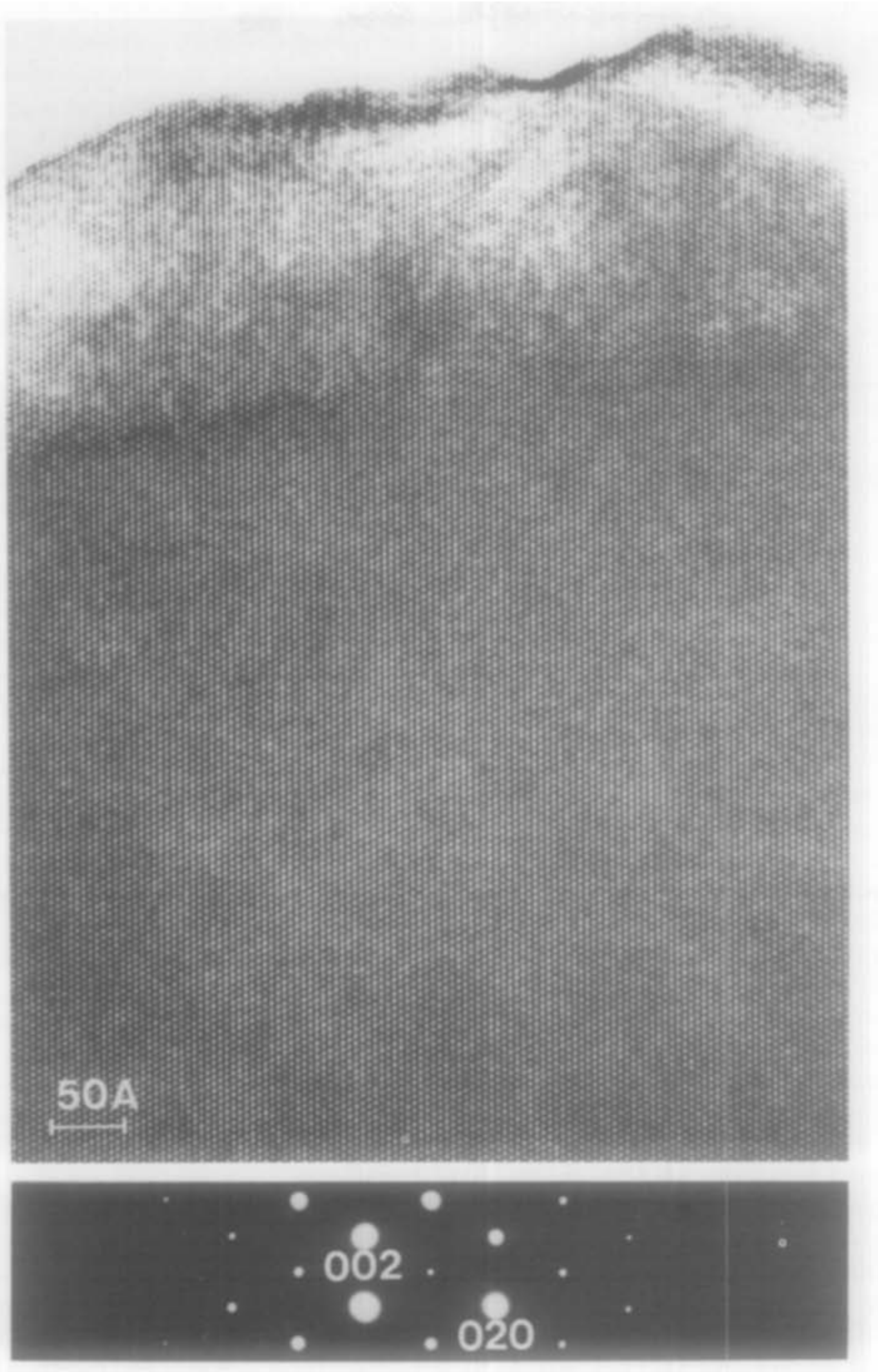

FIG. 3. High resolution electron micrograph of the Cr_2TiO_5 compound with the incident beam parallel to *a*-axis.

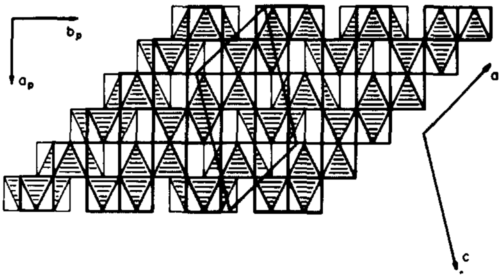

FIG. 4. Idealized structural model for Cr_2TiO_5 viewed down along *b*-axis using representation developed by Andersson and Galy (*12*). Subscript *p* refers to α-PbO_2.

vectorial expressions are as follows;

$$a' = a_{\alpha\text{-}PbO_2} - b_{\alpha\text{-}PbO_2}$$

$$b' = -c_{\alpha\text{-}PbO_2}$$

$$c' = \tfrac{5}{2} b_{\alpha\text{-}PbO_2}.$$

However, the previous expressions were employed in order to define the structure of Cr_2TiO_5 for the present purpose.

The lattice parameters of Cr_2TiO_5 except for *c*-axis were in good agreement with calculated values, $a = 7.10$ Å, $b = 4.91$ Å, $c = 9.46$ Å and $\beta = 112.9°$ (*10*) based on the data from the high pressure form of rutile. The difference in the dimension of *c*-axis between real and idealized structures was reported in the case of the compounds in the series of $(Cr, Fe)_2Ti_{n-2}O_{2n-1}$. The similar reason may also be considered in the present case in which the real structure is expanded by the repulsion between the metal atoms in the face-shared octahedra.

In the present work, information on the positions of atoms and the disorder in the real structure has not been obtained. As reported in the determination of the structure of $CrFeTi_2O_7$ (*7*) by the single crystal X-ray difffaction method, disorder might also take place in the real Cr_2TiO_5 structure due to the existence of a small amount of an intergrowth phase which was detected by electron diffraction in the case of the compound $CrFeTi_2O_7$. However, each thin fragment of the compound Cr_2TiO_5 gave only sharp spots characteristic of a pure phase and the high resolution electron micrograph showed a perfectly well ordered crystal (Fig. 3). An enlarged high resolution electron micrograph is shown in Fig. 5a and the idealized structure viewed down along the *a*-axis is shown for comparison in Fig. 5b. The pseudohexagonal black or white parts separated by 5 Å on the photograph were in good agreement with the idealized structural model. More detailed studies by the electron and X-ray diffraction methods with a single crystal are necessary to determine whether disorder occurs or not in the real structure.

In the lower members of $n \leq 5$ in the series of $Cr_2Ti_{n-2}O_{2n-1}$, Cr_2TiO_5 is a second example existing as a single phase and was confirmed to be isomorphous with V_3O_5 type structure. Thus, the $Cr_2Ti_2O_7$ compound may be regarded as an ordered 1:1 intergrowth phase between Cr_2TiO_5 and TiO_2 (α-PbO_2 structural type). This information is helpful for understanding the nature of the "*E*" phase. In fact, the preliminary electron diffraction study on the *E* phase showed the existence of the ordered intergrowth phases similar to those observed in the series of $(Cr, Fe)_2Ti_{n-2}O_{2n-1}$ or $(Cr, Fe)_{2p}(Ti, Zr)_{p+2q}O_{5p+4q}$ since the electron diffraction patterns of the *E* phase showed several types of superlattice spots additional to the basic structure. Further studies on the nature of the *E* phase are now proceeding.

Finally, the reaction of Cr_2O_3 with $3TiO_2$ above 1300°C was found to result in the formation of the *E* phase and Andersson phase derived from rutile structure. The results showed that the single phase of $Cr_2Ti_3O_9$ ($n = 5$) was never formed. The heat treatment at lower temperature below 1300°C for longer time would be necessary to check on whether $Cr_2Ti_3O_9$ could exist as a single phase or not.

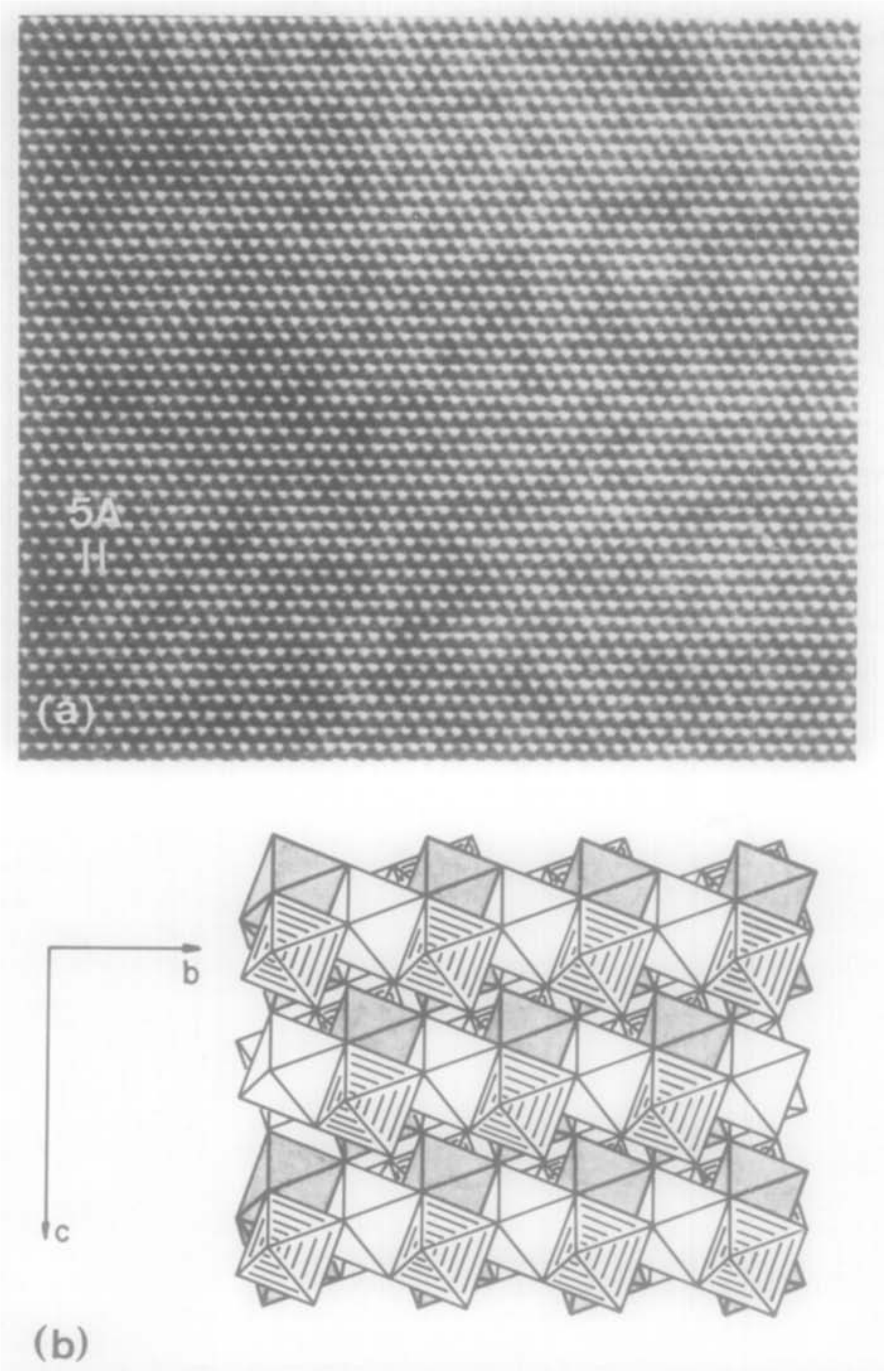

FIG. 5. (a) An enlarged high resolution electron micrograph of the small region as shown in Fig. 3. (b) Idealized projection for the Cr_2TiO_5 structure viewed down along *a*-axis. Shaded octahedra represent a pair of face-shared octahedra and hatched ones are face-shared with the octahedron at the higher or lower level. These pairs of face-shared octahedra separated by 5Å along *b*-axis correspond to black parts in Fig. 5a.

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