

Fig. 2. A general view of the asymmetric unit of hydrated cobalt(II) 4-methyltropolonate (one non-bonded H_2O molecule omitted). Broken lines denote hydrogen bonds.

The asymmetric unit (Fig. 2) consists of a dimer (*A*) with formula $[\text{Co}(\text{MeT})_2\text{H}_2\text{O}]_2$, which has bridging MeT oxygen atoms and is structurally analogous to $[\text{NiT}_2\text{H}_2\text{O}]_2$, and a mononuclear species (*B*) with formula $\text{Co}(\text{MeT})_2(\text{H}_2\text{O})_2$ which exhibits *cis* configuration of water molecules. A non-bonded water molecule is also present. Hydrogen bonds exist between coordinated water molecules and ligand O

atoms; both H_2O molecules of *B* take part in this interaction but only one H_2O on *A* is involved, such that each *B* molecule is associated via three H-bonds (O—O distances 2.61, 2.73 and 2.75 Å) with one *A* molecule only. It is notable that there is no interaction between separate *A* pairs or *B* pairs, other than that induced by normal van der Waals approaches and that many of the shorter intermolecular contacts involve methyl C atoms.

Although the mother liquor must have contained both species, the relative concentration of each, and possibly others, in solution could have been a structure-determining factor for the solid state. However, the observed constitution of the stable lattice (the crystals were not moisture sensitive) would appear necessary to facilitate H-bonding and lattice packing which, because of the methyl substituent, is possibly not so efficiently achieved when either species is absent.

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Electron-density distribution in rutile crystals. By H. SHINTANI, S. SATO and Y. SAITO, *Institute for Solid State Physics, University of Tokyo, Roppongi-7, Minato-ku, Tokyo 106, Japan*

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The distribution of residual electron density in rutile crystals has been calculated from intensities carefully obtained by diffractometry. There is no indication that the charge densities of Ti^{4+} (having no *d* electrons) are deformed in an octahedral crystal field. This result seems to support our conclusion that the aspherical charge densities of Ni^{2+} ($3d^8$) in $\gamma\text{-Ni}_2\text{SiO}_4$ are due to *d* electrons placed in an octahedral crystal field.

An indication of $3d$ electrons in the t_{2g} orbitals of Ni^{2+} and Co^{3+} was observed in the final difference syntheses of $\gamma\text{-Ni}_2\text{SiO}_4$ and $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$ (Marumo, Isobe, Saito, Yagi & Akimoto, 1974; Iwata & Saito, 1973). In the difference maps eight small peaks were arranged at the corners of a cube around the transition metal atom, the peaks being at 0.45 Å from the metal atom. To see whether or not such peaks are due to *d* electrons, a difference synthesis of rutile, TiO_2 , was calculated based on carefully measured intensity data, since Ti^{4+} possesses no $3d$ electrons.

All attempts to shape a crystal specimen into a sphere failed. The specimen used had the dimensions $0.08 \times 0.08 \times 0.09$ mm. The intensities were collected on a Rigaku automated four-circle diffractometer. The experimental conditions were exactly the same as those for $\gamma\text{-Ni}_2\text{SiO}_4$,

Table 1. *Crystal data and atomic parameters*

$\text{TiO}_{2-\alpha}$, $\alpha = 0.016$ (7)	$U = 62.072 \text{ \AA}^3$ at 26°C
Tetragonal, $P4_2/mnm$	$D_m = 4.264 \text{ g cm}^{-3}$
$a = 4.5845$ (1) Å	$D_x = 4.260 \text{ g cm}^{-3}$
$c = 2.9533$ (1) Å	$Z = 2$

O at $(0, u, u)$ with $u = 0.30493$ (7)
 Isotropic extinction parameter $g = 0.29 \times 10^4$

The temperature factors are in the form:

$$\exp \{ -2\pi^2(h^2 a^{*2} U_{11} + k^2 b^{*2} U_{22} + l^2 c^{*2} U_{33} + 2hka^* b^* U_{12} + 2hla^* c^* U_{13} + 2klb^* c^* U_{23}) \}$$

	$U_{11} = U_{22}$	U_{33}	U_{12}	U_{13}	U_{23}	($\times 10^5$)
Ti	699 (4)	467 (4)	-31 (9)	0	0	
O	601 (9)	454 (11)	-372 (22)	0	0	

Table 2. Observed and calculated structure amplitudes

h	k	l	FO		FC		h	k	l	FO		FC		h	k	l	FO		FC		h	k	l	FO		FC	
			Obs.	Calc.	Obs.	Calc.				Obs.	Calc.	Obs.	Calc.				Obs.	Calc.	Obs.	Calc.				Obs.	Calc.		
0	0	0	53.44	52.56	0	0	0	7.73	7.86	7	0	0	47.74	47.84													
0	0	1	80.59	81.27	0	1	1	13.84	14.02	8	0	0	22.14	22.21													
0	0	2	88.70	89.04	0	2	2	18.32	18.48	9	0	0	17.73	17.80													
0	0	3	59.28	59.91	0	3	3	11.64	11.74	10	0	0	13.50	13.57													
0	0	4	33.56	33.66	0	4	4	7.56	7.64	11	0	0	10.00	10.07													
0	0	5	24.76	24.83	0	5	5	5.64	5.71	12	0	0	7.84	7.91													
0	0	6	18.40	18.46	0	6	6	4.32	4.38	13	0	0	6.24	6.31													
0	0	7	13.72	13.77	0	7	7	3.24	3.29	14	0	0	5.12	5.17													
0	0	8	10.36	10.40	0	8	8	2.36	2.40	15	0	0	4.24	4.29													
0	0	9	8.00	8.03	0	9	9	1.68	1.71	16	0	0	3.52	3.55													
0	0	10	6.64	6.66	0	10	10	1.16	1.18	17	0	0	2.96	2.99													
0	0	11	5.44	5.45	0	11	11	0.80	0.81	18	0	0	2.56	2.57													
0	0	12	4.40	4.41	0	12	12	0.56	0.57	19	0	0	2.24	2.25													
0	0	13	3.52	3.53	0	13	13	0.40	0.41	20	0	0	1.96	1.97													
0	0	14	2.80	2.81	0	14	14	0.28	0.29	21	0	0	1.72	1.73													
0	0	15	2.24	2.25	0	15	15	0.19	0.20	22	0	0	1.52	1.53													
0	0	16	1.76	1.77	0	16	16	0.14	0.15	23	0	0	1.36	1.37													
0	0	17	1.36	1.37	0	17	17	0.10	0.11	24	0	0	1.24	1.25													
0	0	18	1.04	1.05	0	18	18	0.07	0.08	25	0	0	1.16	1.17													
0	0	19	0.80	0.81	0	19	19	0.05	0.06	26	0	0	1.12	1.13													
0	0	20	0.64	0.65	0	20	20	0.04	0.04	27	0	0	1.08	1.09													
0	0	21	0.52	0.53	0	21	21	0.03	0.03	28	0	0	1.04	1.05													
0	0	22	0.40	0.41	0	22	22	0.02	0.02	29	0	0	1.00	1.01													
0	0	23	0.32	0.33	0	23	23	0.02	0.02	30	0	0	0.96	0.97													
0	0	24	0.24	0.25	0	24	24	0.01	0.01	31	0	0	0.92	0.93													
0	0	25	0.19	0.20	0	25	25	0.01	0.01	32	0	0	0.88	0.89													
0	0	26	0.14	0.15	0	26	26	0.01	0.01	33	0	0	0.84	0.85													
0	0	27	0.10	0.11	0	27	27	0.01	0.01	34	0	0	0.80	0.81													
0	0	28	0.08	0.08	0	28	28	0.01	0.01	35	0	0	0.76	0.77													
0	0	29	0.06	0.07	0	29	29	0.01	0.01	36	0	0	0.72	0.73													
0	0	30	0.05	0.05	0	30	30	0.01	0.01	37	0	0	0.68	0.69													
0	0	31	0.04	0.04	0	31	31	0.01	0.01	38	0	0	0.64	0.65													
0	0	32	0.03	0.03	0	32	32	0.01	0.01	39	0	0	0.60	0.61													
0	0	33	0.02	0.03	0	33	33	0.01	0.01	40	0	0	0.56	0.57													
0	0	34	0.02	0.02	0	34	34	0.01	0.01	41	0	0	0.52	0.53													
0	0	35	0.01	0.02	0	35	35	0.01	0.01	42	0	0	0.48	0.49													
0	0	36	0.01	0.01	0	36	36	0.01	0.01	43	0	0	0.44	0.45													
0	0	37	0.01	0.01	0	37	37	0.01	0.01	44	0	0	0.40	0.41													
0	0	38	0.01	0.01	0	38	38	0.01	0.01	45	0	0	0.36	0.37													
0	0	39	0.01	0.01	0	39	39	0.01	0.01	46	0	0	0.32	0.33													
0	0	40	0.01	0.01	0	40	40	0.01	0.01	47	0	0	0.28	0.29													
0	0	41	0.01	0.01	0	41	41	0.01	0.01	48	0	0	0.24	0.25													
0	0	42	0.01	0.01	0	42	42	0.01	0.01	49	0	0	0.20	0.21													
0	0	43	0.01	0.01	0	43	43	0.01	0.01	50	0	0	0.16	0.17													
0	0	44	0.01	0.01	0	44	44	0.01	0.01	51	0	0	0.12	0.13													
0	0	45	0.01	0.01	0	45	45	0.01	0.01	52	0	0	0.08	0.09													
0	0	46	0.01	0.01	0	46	46	0.01	0.01	53	0	0	0.04	0.05													
0	0	47	0.01	0.01	0	47	47	0.01	0.01	54	0	0	0.00	0.01													
0	0	48	0.01	0.01	0	48	48	0.01	0.01	55	0	0	0.00	0.01													
0	0	49	0.01	0.01	0	49	49	0.01	0.01	56	0	0	0.00	0.01													
0	0	50	0.01	0.01	0	50	50	0.01	0.01	57	0	0	0.00	0.01													
0	0	51	0.01	0.01	0	51	51	0.01	0.01	58	0	0	0.00	0.01													
0	0	52	0.01	0.01	0	52	52	0.01	0.01	59	0	0	0.00	0.01													
0	0	53	0.01	0.01	0	53	53	0.01	0.01	60	0	0	0.00	0.01													

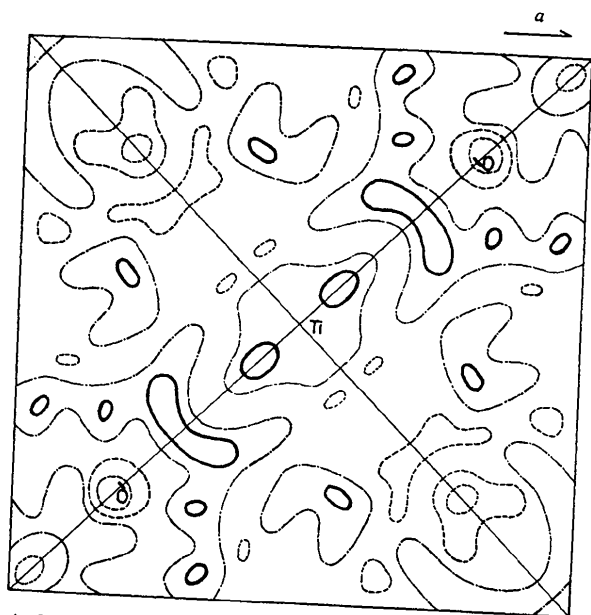


Fig. 1. Section of the difference Fourier function through the titanium ion and perpendicular to the *c* axis. Contours are at intervals of 0.2 e⁻³. Negative contours are broken lines, zero contours chained.

except that the maximum number of repetitions of a measurement was ten. Equivalent reflexions *hkl* and *h \bar{k} l* were measured and averaged. In all, 302 independent data were collected and then corrected for Lorentz-polarization and absorption. The structure was refined by the full-matrix least-squares program *LINUS* (Coppens & Hamilton, 1970). The site-occupancy parameter, α , in the formulation TiO_{2-x} was also refined. The final *R* value was reduced to 0.010 and *R_w* was 0.014 for the 302 observed reflexions. The atomic scattering factors for Ti^{4+} and O^{2-} were taken from Fukamachi (1971).

The crystal data and the final atomic parameters are listed in Table 1. The *u* parameter of 0.30493 (7) agrees well with the previously obtained value, 0.30479 (10), within experimental error (Abrahams & Bernstein, 1971). The observed and calculated structure amplitudes are compared

in Table 2. The final difference syntheses were calculated and a section through the titanium ion and perpendicular to the *c* axis is shown in Fig. 1. The resulting maps were featureless to within 0.3 e⁻³. There were no meaningful peaks around the titanium atom, indicating that the charge density around the Ti^{4+} is spherical, as expected. This seems to support our result previously obtained for $\gamma-Ni_2SiO_4$.

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