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Electron-Density Distribution in Crystals of γ -Ni₂SiO₄

BY F. MARUMO[†] AND M. ISOBE

Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan

AND Y. SAITO, T. YAGI AND S. AKIMOTO

The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan

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The electron-density distribution in γ -Ni₂SiO₄ has been calculated on the basis of carefully measured intensity data collected by diffractometry with Mo $K\alpha$ radiation. There was an indication in the final difference Fourier maps that the charge densities of the nickel atom were deformed in an octahedral crystal field. Residual electron densities were observed between Si and O atoms.

Introduction

In the final difference synthesis of [Co(NH₃)₆][Co(CN)₆], eight peaks with heights of about 0.3 e Å⁻³ were arranged at the corners of a cube around the cobalt atom, the peaks being at 0.45 Å from the cobalt atom (Iwata & Saito, 1973). These peaks were suspected of being an indication of 3d electrons in the *t*_{2g} orbitals of the cobalt. This point must be examined in detail with reference to other transition-metal complexes. Crystals of γ -Ni₂SiO₄ have a strictly normal spinel structure with the cell dimension $a = 8.044$ (1) Å and the symmetry *Fd*3*m* (Yagi, Marumo & Akimoto, 1974). They were used for a close examination of the residual electron-density because the crystals are suitable for diffractometry and have only one positional parameter to be determined.

Experimental

A crystal specimen shaped into a sphere of about 0.08 mm diameter was used for X-ray work. The intensity data were collected on a Rigaku automated four-circle diffractometer. The experimental conditions were

broadly similar to those described in the previous paper (Iwata & Saito, 1973). The ω -2 θ scan technique was employed with a scanning speed of 2° min⁻¹ in ω , using Mo $K\alpha$ radiation monochromated by a graphite plate. Scanning range was calculated from the formula $1.5 + 0.8^\circ \times \tan \theta$. If the value of $\sigma(|F|)/|F|$ was greater than 0.0025, the measurement was automatically repeated until $\sigma(|F|)/|F|$ became less than 0.0025, where $\sigma(|F|)$ is the standard deviation of $|F|$ due to the counting statistics. The maximum number of repetitions was limited to eight. Reflexions with $h \geq k \geq 0$ and $l \geq 0$ were measured up to a 2θ value of 135°. Three symmetry-related reflexions are contained in this range for reflexions with general indices, two for *hhl* and one for *hhh*. The *hhh* reflexions were also measured in order to check for accidental errors in *F(hhh)*. For the structure refinement and the electron-density calculation, reflexions in the range $l \geq h \geq k$ were used, excluding weak ones whose $|F|$ was smaller than $3\sigma(|F|)$. In total, 210 independent data were collected. The intensities were corrected for Lorentz, polarization and absorption effects. The structure was refined by the full-matrix least-squares program *LINUS* (Coppens & Hamilton, 1970) by assuming isotropic extinction. The

Table 1. *Final atomic coordinates* ($\times 10^4$) *and thermal parameters* ($\times 10^5$)

The temperature factors are in the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	6250	6250	6250	132 (1)	132 (1)	132 (1)	-9 (3)	-9 (3)	-9 (3)
Si	0	0	0	109 (4)	109 (4)	109 (4)	0	0	0
O	3689 (1)	3689 (1)	3689 (1)	152 (4)	152 (4)	152 (4)	-17 (11)	-17 (11)	-17 (11)

final R value was 0.017 and the R_w became 0.018 for the 210 observed reflexions. Unit weight was given to all the reflexions. The atomic scattering factors and dispersion corrections for Ni^{2+} and Si^{4+} ions were taken from *International Tables for X-ray Crystallography* (1962). For O^{2-} ions, the scattering factors given by Tokonami (1965) were used without dispersion correction. The final atomic parameters are listed in Table 1. The observed and calculated structure factors are given in Table 2.

Table 2. Observed and calculated structure amplitudes

h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c
0	0	4	418.39	416.65	7	1	11	83.86	93.45	5	3	11	81.17	84.02	9	5	9	53.49	52.18
0	0	8	308.58	307.96	7	1	11	97.94	96.22	5	3	11	54.10	55.04	9	5	11	31.41	31.31
0	0	12	127.14	130.50	7	1	15	38.42	39.05	5	3	15	35.71	37.10	9	5	13	14.86	15.70
0	0	16	132.19	125.17	7	1	19	29.97	27.53	5	3	19	43.10	44.40	9	5	15	47.10	45.86
0	0	20	62.74	64.46	7	1	19	45.61	45.94	5	3	19	146.08	133.45	9	5	17	65.72	60.61
2	0	2	82.05	76.16	7	1	11	66.20	65.41	7	3	9	83.85	84.07	11	5	11	65.42	64.02
2	0	4	55.00	56.16	7	1	13	42.86	42.52	7	3	11	60.36	61.62	11	5	13	29.14	28.60
2	0	6	17.31	17.34	7	1	15	30.72	30.44	7	3	13	39.46	30.43	11	5	15	32.18	31.39
2	0	8	13.76	14.04	7	1	17	23.85	27.47	7	3	15	36.36	61.62	11	5	17	24.24	24.38
2	0	10	13.76	14.04	7	1	19	42.03	41.73	7	3	17	39.88	39.75	11	5	19	29.14	28.60
2	0	12	4.31	3.24	7	1	21	25.85	27.47	7	3	19	36.36	61.62	11	5	19	24.24	24.38
2	0	14	167.36	165.93	7	1	23	53.23	51.94	9	3	9	61.84	62.19	6	6	6	102.07	101.07
2	0	16	174.24	173.32	7	1	25	40.93	39.59	9	3	11	31.37	36.88	6	6	8	31.49	31.45
2	0	18	95.95	87.98	7	1	27	14.28	14.63	9	3	13	20.12	20.88	6	6	10	76.11	76.78
2	0	20	41.50	41.50	7	1	29	10.93	10.93	9	3	15	10.93	10.93	6	6	12	18.94	18.96
2	0	22	47.50	47.35	7	1	31	165.80	168.01	9	3	17	31.61	31.35	6	6	14	43.13	46.36
2	0	24	27.50	27.32	7	1	33	164.38	163.25	11	3	11	67.70	67.26	6	6	16	64.18	61.02
2	0	26	20.91	21.39	7	1	35	55.55	55.20	11	3	13	37.20	35.18	6	6	18	53.66	51.80
2	0	28	105.26	104.88	7	1	37	40.93	40.65	11	3	15	25.42	25.61	6	6	20	39.87	39.76
2	0	30	105.26	104.88	7	1	39	26.46	27.22	11	3	17	34.47	33.63	7	7	7	55.27	55.32
2	0	32	117.64	118.85	7	1	41	64.25	69.55	11	3	19	26.46	26.61	7	7	9	65.00	62.65
2	0	34	66.43	64.56	7	1	43	49.16	51.88	4	4	4	252.86	251.97	7	7	11	74.64	74.22
2	0	36	124.34	124.34	7	1	45	51.97	50.98	4	4	6	241.42	243.02	7	7	13	55.07	51.86
2	0	38	126.54	129.49	7	1	47	31.80	31.89	4	4	8	114.52	115.79	7	7	15	38.03	37.82
2	0	40	236.36	235.34	7	1	49	21.44	20.94	4	4	10	111.21	114.57	7	7	17	21.13	22.10
2	0	42	170.25	171.79	7	1	51	123.72	122.49	4	4	12	57.47	60.14	9	7	19	62.35	59.54
2	0	44	81.02	80.76	7	1	53	37.42	35.96	4	4	14	39.44	38.27	9	7	21	40.92	41.98
2	0	46	43.34	44.21	7	1	55	85.50	86.91	4	4	16	115.55	119.86	7	13	23	40.92	41.98
2	0	48	46.25	46.25	7	1	57	24.51	23.65	6	6	18	11.38	14.98	9	7	25	28.14	29.75
2	0	50	139.23	139.77	7	1	59	13.76	14.36	6	6	20	134.78	130.54	11	7	27	20.95	15.11
2	0	52	124.31	123.64	7	1	61	64.75	69.55	8	8	22	118.60	119.02	11	7	29	40.31	40.79
2	0	54	58.31	61.83	7	1	63	26.81	25.89	8	8	24	75.17	74.82	11	7	31	28.23	27.41
2	0	56	46.25	46.25	7	1	65	46.75	46.32	8	8	26	75.17	74.82	11	7	33	48.62	48.60
2	0	58	100.46	101.95	7	1	67	18.94	16.92	10	10	28	26.58	16.69	11	7	35	18.08	17.45
2	0	60	148.86	149.55	7	1	69	64.78	69.49	10	10	30	18.08	17.37	8	8	37	154.42	154.57
2	0	62	81.02	82.59	7	1	71	12.95	12.34	12	12	32	85.58	85.36	8	8	39	87.74	88.06
2	0	64	37.99	37.48	7	1	73	35.49	35.39	12	12	34	82.21	81.04	8	8	41	87.88	89.31
2	0	66	131.86	129.35	7	1	75	14.31	13.15	12	12	36	104.99	103.61	10	10	43	18.26	18.27
2	0	68	52.79	56.81	7	1	77	20.78	20.71	12	12	38	74.82	73.89	12	12	45	96.85	96.58
2	0	70	39.40	41.25	7	1	79	46.75	46.32	12	12	40	27.74	27.70	9	9	47	48.62	48.01
2	0	72	32.26	31.97	7	1	81	159.24	160.72	12	12	42	46.55	46.51	9	9	49	21.37	23.64
2	0	74	58.77	56.50	7	1	83	77.84	78.58	12	12	44	71.63	73.89	11	11	51	10.78	10.54
2	0	76	122.81	122.79	7	1	85	47.39	48.06	12	12	46	13.34	14.40	11	11	53	21.08	21.21
2	0	78	85.14	84.84	7	1	87	35.49	35.49	12	12	48	85.73	85.73	11	11	55	39.05	41.48
2	0	80	43.55	44.81	7	1	89	60.58	63.27	7	7	50	98.52	97.52	10	10	57	56.00	55.39
2	0	82	25.17	25.95	7	1	91	22.02	22.51	7	7	52	72.02	72.02	10	10	59	49.99	46.30
2	0	84	59.32	60.36	7	1	93	12.95	12.95	7	7	54	25.76	25.79	10	11	61	51.28	51.1
2	0	86	38.53	38.69	7	1	95	129.85	128.60	7	7	56	45.82	42.99	11	11	63	41.19	40.17
2	0	88	28.25	28.70	5	3	7	61.00	61.28	7	5	17	34.40	35.75	12	12	65	60.10	60.27
2	0	90	81.00	82.81	5	3	9	36.17	35.75	7	5	19	29.69	27.55					

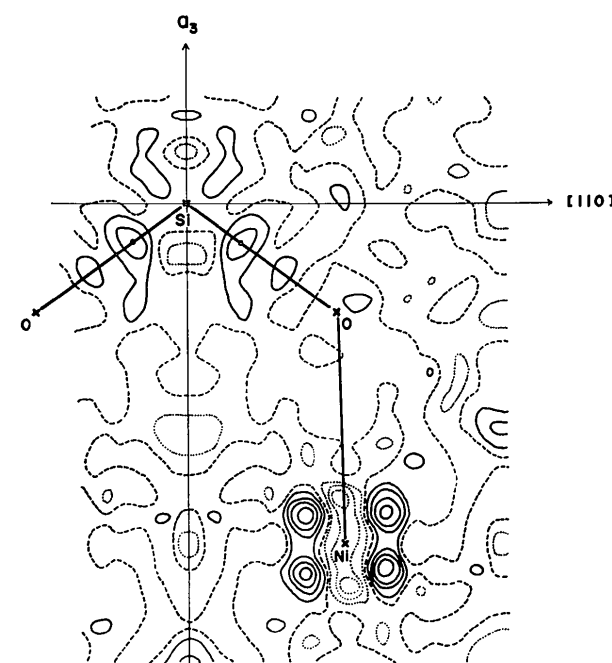


Fig. 1. The section of the difference Fourier function through the plane $y=x$. Contours are at the interval of $0.2 e \text{ \AA}^{-3}$. Zero contours are in broken lines, and negative contours dotted.

Results and discussion

The u parameter of 0.3689 (1) agrees well with the previously obtained value, 0.3687 (2), within experimental error (Yagi *et al.*, 1974). The smaller extinction effect ($g=0.075 \times 10^4$) in the present study is probably due to the shaping treatment of the specimen. The site-occupancy parameter, α , in the expression $(Ni_{2-\alpha}, Si_{\alpha})(Si_{1-\alpha}, Ni_{\alpha})O_4$ was also refined, converging to 0.013 (6), indicating that the crystal is practically a pure normal spinel as in the case of the specimen used in the previous study (Yagi *et al.*, 1974).

A section of the difference Fourier map through the plane $y=x$ is shown in Fig. 1. All the crystallographically independent atoms and chemical bonds in the spinel structure appear in this section. Each Ni-O bond is approximately parallel to one of the $\langle 100 \rangle$ directions, and the Si-O are exactly in the $\langle 111 \rangle$ directions. A remarkable feature of the map is the existence of four salient peaks 0.46 \AA from the nickel atom. In the three-dimensional maps, there are eight such peaks around the nickel atom, of which two are crystallographically independent. The height of the peak on the threefold rotation axis of the crystal is $0.9 e \text{ \AA}^{-3}$ and the other, $1.0 e \text{ \AA}^{-3}$. These eight peaks are disposed at the eight corners of a cube surrounding the nickel atom. Since the Ni^{2+} ion is placed in a nearly octahedral field, six out of the eight $3d$ electrons of the ion are in the t_{2g} orbitals and two are in the e_g orbitals in the ground state. The electron-density distribution is, therefore, expected to be extended specifically along the body-diagonals with respect to the Ni-O bonds, losing the spherical symmetry of the free ion. The observed peaks are probably attributable to this asphericity in the density distribution of $3d$ electrons. A nickel atom in an octahedral site might vibrate with respect to the Ni-O bonds than along the bonds. Such thermal vibration would also give rise to the feature mentioned above. This effect might not be serious in the case of ionic crystals like spinels with rather small temperature factors (r.m.s.d. for the nickel atom: 0.066 \AA). Neutron diffraction studies are required to settle this point.

In the Fourier series of the difference synthesis, many of the Fourier coefficients were smaller than $\sigma(|F(hkl)|)$. Therefore, summation was also carried out by selecting terms which satisfied the following two conditions: (1) $|\Delta F(hkl)| \geq 2\sigma(|F(hkl)|)$, and (2) $\Delta F(hkl) \geq 2(|F_o(hkl)| - |F'_o(hkl)|)$ if $\Delta F(hkl) \geq 0$ and $\Delta F(hkl) \leq 2(|F_o(hkl)| - |F'_o(hkl)|)$ if $\Delta F(hkl) < 0$. Here, $|F_o(hkl)|$ is the structure amplitude of the reflexion adopted in the present study, $|F'_o(hkl)|$ the mean structure amplitude of observed reflexions which are equivalent to hkl but unused, and $\Delta F(hkl) = |F_o(hkl)| - |F'_o(hkl)|$. The second condition was introduced in order to exclude the reflexions from the summation for which $|\Delta F(hkl)|$'s were large owing to accidental errors. There were 39 reflexions which satisfied the

above conditions. The result is shown in Fig. 2. Four well defined peaks are observed at the same positions as in Fig. 1, which is based on all the reflexions, suggesting the significance of the peaks around the nickel atom.

Similar residual densities were observed in the difference Fourier maps of [Co(NH₃)₆][Co(CN)₆] by Iwata & Saito (1973) and also in those of C₆H₆Cr(CO)₃ by Rees & Coppens (1973) around the transition-metal atoms. In the case of [Co(NH₃)₆][Co(CN)₆], peaks are at distances of 0.45 Å from the cobalt atom with the maximum density of 0.3 e Å⁻³. The asphericity appears to be smeared out owing to the larger thermal vibration, giving the smaller residual densities. It may be advantageous to use crystals with small thermal vibration for observing asphericity in electron-density distributions of transition metals.

In Fig. 1, a peak with height 0.6 e Å⁻³ is observed at 0.61 Å from the silicon atom on the Si–O bond. This might be due to the covalent character of the Si–O bond. There exists a subsidiary maximum on the bond at 0.63 Å from the oxygen atom. The height of 0.35 e Å⁻³ is, however, too low to give any significance to the peak. It is of interest that the residual densities around the nickel atom are much larger than those for the Si–O bonding electrons. Investigation of silicates of second-row elements, such as sodium, magnesium and aluminum, is desirable to obtain information about the Si–O bonding electrons.

The calculations were performed on a HITAC 8700 computer at The Computer Centre of Tokyo Institute of Technology, and partly on a FACOM 270-30 computer at The Institute for Solid State Physics. This research was aided by a Scientific Research Grant from the Ministry of Education, to which the authors' thanks are due.

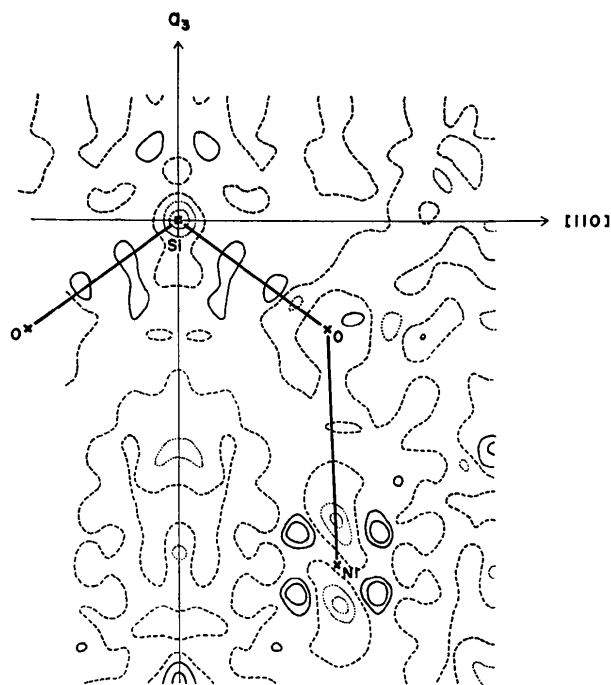


Fig. 2. A section of the difference Fourier map synthesized with 39 selected terms. Contours are at intervals of 0.2 e Å⁻³. Zero and negative contours are in broken and dotted lines, respectively.

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