

## Disordered Structure of $\beta_{II}$ -Li<sub>2</sub>CoSiO<sub>4</sub>

BY YOSHITO TAKAKI

*Department of Physics, Osaka Kyoiku University, Tennoji, Osaka 543, Japan*

AND HIROSHI YAMAGUCHI

*Department of Earth Science (Mineralogy), Osaka Kyoiku University, Tennoji, Osaka 543, Japan*

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### Abstract

Crystals of the title compound give diffraction patterns of sharp ( $k$  even) and diffuse ( $k$  odd) X-ray reflections. These diffuse reflections are broadened along  $b^*$ , suggesting one-dimensional disorder along  $b$ . The disordered structure is satisfactorily described in terms of multiple twinning of two twin components  $PQ$  and  $QP$  in equal proportions, where  $P$  and  $Q$  are subcells of the structure of  $\beta_{II}$ -Li<sub>2</sub>CoSiO<sub>4</sub>. The occurrence of a remarkably high peak for the Li(1) atom found on a Fourier map is explained in terms of the superposition of a ghost due to truncation errors in the integrated intensity measurements of diffuse reflections.

### Introduction

In the course of a structural investigation of  $\beta_{II}$ -Li<sub>2</sub>CoSiO<sub>4</sub>, Yamaguchi, Akatsuka, Setoguchi & Takaki (1979), hereinafter YAST, found that the temperature factor of Li(1) was very small and the peak density of this atom was noticeably larger than that of Li(2). At this stage it was thought that the occurrence of the large peak height would be closely related to the disordering of the structure which was expected from the observation of diffuse reflections. Therefore, in this paper we deal with an investigation of a disordered structure of  $\beta_{II}$ -Li<sub>2</sub>CoSiO<sub>4</sub> and give an interpretation of the occurrence of the high peak of the Li(1) atom.

### Experimental

Crystal data reported by YAST (1979) are:  $a = 6.253$  (5),  $b = 10.685$  (9),  $c = 4.929$  (9) Å, space group  $Pbn2_1$ ,  $Z = 4$ .

Weissenberg photographs of 17 crystals examined showed that all reflections with  $k$  odd are significantly broadened along  $b^*$ ; the degree of diffuseness was found to vary from crystal to crystal. Of these, the crystal used for structure determination by YAST

showed a very slight elongation of diffuse reflections; it seemed at first sight as if they were sharp spots. A quantitative study of the disordered structure was made by using another crystal which showed considerable elongation of diffuse reflections. Intensities were measured with a microdensitometer (MD-II, Mitaka-Koki Co.) on  $hk0$  Weissenberg photographs taken with graphite-monochromated Mo  $K\alpha$  radiation.

### Disordered structure of $\beta_{II}$ -Li<sub>2</sub>CoSiO<sub>4</sub>

The observation of the diffuse scattering in the *Experimental* indicates the existence of one-dimensional disorder along  $b$ . A typical example of such disorder is given by Wilson (1962). In the present case, the disorder can be expressed in terms of a disordered arrangement of equal proportions of two kinds of layers, each having a dimension  $b'$  ( $= b/2$ ) and consisting of ordered arrangements of a component along  $a$  and  $c$ . From this point of view we examined the structure given by YAST and found the two basic components,  $P$  and  $Q$ , which are subcells of the above

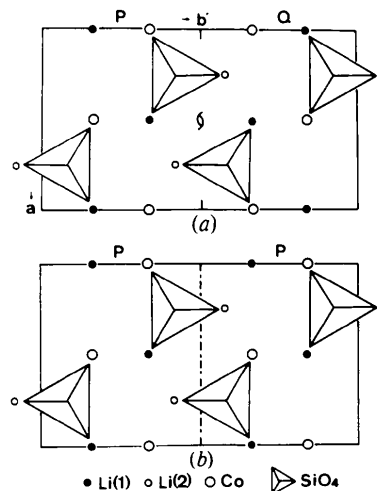


Fig. 1. Schematic representation of the double units, (a)  $PQ$  and (b)  $PP$ , viewed along  $c$ .

original structure (Fig. 1). The fractional coordinates of atoms in these two components may be represented by

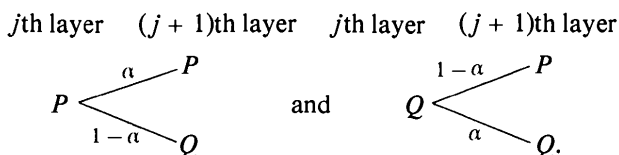
$$P: x, y', z; \frac{1}{2} + x, 1 - y', \frac{1}{2} + z;$$

$$Q: \frac{1}{2} - x, y', z; 1 - x, 1 - y', \frac{1}{2} + z;$$

where the coordinate  $y'$  is referred to  $b'$ .

The original structure is then described by a sequence  $PQPQ\dots$ , where the symmetry element relating one component to the next is  $2_1$  parallel to  $c$ . That is,  $Q$  (or  $P$ ) is generated from the preceding component  $P$  (or  $Q$ ) by the  $2_1$  operation. Similarly we found that  $P$  (or  $Q$ ) can also be generated from the preceding component  $P$  (or  $Q$ ) by the  $n$  glide operation without difficulties in the interatomic contacts at the boundary, the glide plane being normal to  $b'$ . Note that the packing of the O atoms is almost unaffected by the above two symmetry operations.

A model for the arrangement of the two components along  $b'$  may be obtained by assuming that if the  $j$ th component is  $P$  (or  $Q$ ), the probability of the  $(j + 1)$ th component being  $Q$  (or  $P$ ) is  $1 - \alpha$ , and of the component being  $P$  (or  $Q$ ) is  $\alpha$ . The probability trees for this model are given as follows:



Let a coordinate in reciprocal space along  $b'^*$  be  $\eta$ ; then the diffracted intensity for  $h\eta l$  is given by (Wilson, 1962)

$$I = \frac{1}{4} I_e N_1^2 N_2^2 [ |P + Q|^2 G(\eta) + N_2 |P - Q|^2 D(\eta) ], \quad (1)$$

with

$$G(\eta) = \sin^2 N_2 \pi \eta / \sin^2 \pi \eta$$

and

$$D(\eta) = (1 - x^2) / (1 + x^2 - 2x \cos 2\pi \eta),$$

where  $x = 2\alpha - 1$ ;  $I_e$  is the scattered intensity from a single electron;  $N_1, N_2, N_3$  are numbers of subcells along  $a, b'$  and  $c$  respectively;  $P$  and  $Q$  are structure factors for  $h\eta l$  and are calculated from  $\sum_j f_j \exp 2\pi i (hx_j + \eta y'_j + lz_j)$ . Note that hereinafter indices  $k$  and  $k'$  are referred to  $b$  and  $b'$  respectively.

From equation (1) it can be seen that the first term gives intensities of sharp reflections with  $k$  even ( $k'$  integer) from the averaged structure of  $P$  and  $Q$ , and the second gives those of diffuse reflections associated with a reciprocal-lattice point with  $k$  odd ( $k'$  half integer). The intensities of diffuse maxima are proportional to those of the corresponding reflections given by the  $PQ$  cell, and the profiles go on becoming sharper and higher as  $\alpha$  approaches zero.

Equation (1) explains qualitatively the observed diffraction patterns, suggesting that the above disorder model is essentially correct. Further detailed examination of the disordered structure was carried out by comparing observed and calculated intensities for the diffuse 110 reflection, a crystal showing considerable elongation of diffuse reflections being used for the examination. A correction for instrumental broadening was applied to the calculated intensities by the following procedure.

Suppose that a crystal giving instrumental broadening alone gives an intensity  $g(s)$  at a distance  $s$  along  $b'^*$  from the peak of a diffuse spot, and suppose that a crystal giving intrinsic broadening, when photographed under the ideal condition of no instrumental broadening, gives an intensity distribution defined by  $f(s)$ . Then the intensity distribution broadened by the above two causes may be given by (Jones, 1938)

$$I_D(\eta) = \int f(s) g(\eta - s) ds, \quad (2)$$

where the integral is taken over all values of  $s$  for which  $f(s)g(\eta - s)$  is different from zero, and  $g(s)$  is normalized by writing

$$\int g(s) ds = 1.$$

The functions  $f(s)$  and  $g(s)$  were obtained as follows: the observation of diffuse reflections obviously indicated that broadening due to disorder accounts for most of the total intrinsic broadening. Thus  $f(s)$  is in the form

$$f(s) = \frac{1}{4} I_e N_1^2 N_2^2 N_3^2 |P - Q|^2 (1 - x^2) / (1 + x^2 - 2x \cos 2\pi s). \quad (3)$$

The instrumental broadening  $g(s)$  was in the form of an experimental intensity curve (Jones, 1938) along  $b'^*$  obtained from a microdensitometer trace of the 110 spot on a photograph of the crystal used in this study taken by the stationary-crystal method (Flack, 1970).

By applying numerical integration to equation (2), the intensities for the diffuse 110 reflection were

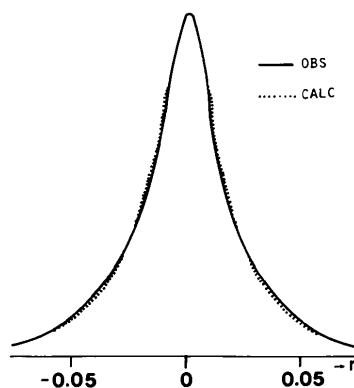


Fig. 2. Observed and calculated intensity curves (arbitrary scale) for the diffuse 110 reflection.

calculated for various values of  $\alpha$ , and the best agreement between observed and calculated intensities was obtained with the value of  $\alpha = 0.045$  as shown in Fig. 2. The probabilities of finding double units  $PQ$ ,  $QP$ ,  $PP$  and  $QQ$  in the crystal are then 0.48, 0.48, 0.02 and 0.02 respectively. This indicates that the crystal structure mainly consists of two predominant sequences,  $PQPQ\dots$  and  $QPQP\dots$ , or it may be said that the disordered structure can be satisfactorily explained in terms of multiple twinning of the two twin components  $PQ$  and  $QP$  in equal proportions.

### Interpretation of the high peak of Li(1)

As has been described in the *Experimental*, the crystal used for the structure determination showed very slight elongation of diffuse reflections, and all intensity data were collected with a four-circle diffractometer [ $2\theta/\omega$  scan technique with the scan range  $(1.2 + 0.5 \tan \theta)^\circ$  and a receiving slit with an aperture of  $3.5 \times 3.5$  mm]. Therefore, we first considered an ideal case where the intensities of sharp and diffuse reflections were completely integrated, giving

$$I_L = \frac{C}{4} N_1 N_2 N_3 |P + Q|^2$$

and

$$\begin{aligned} I_D &= \frac{C}{4} N_1 N_2 N_3 \int_{k'-\frac{1}{2}}^{k'+\frac{1}{2}} |P - Q|^2 D(\eta) d\eta \\ &= \frac{C}{4} N_1 N_2 N_3 |P - Q|^2, \end{aligned}$$

where  $C$  is a constant. These expressions show the intensities corresponding to the integrated diffraction intensities given by the regular sequence of the  $PQ$  cell, and therefore no ghost due to disorder may be observed on a Fourier map. In the above calculation we took  $|P - Q|^2$  as constant since diffuse intensities were distributed in a small region about a lattice point, and in addition the variation of  $|P - Q|^2$  was much slower than that of  $D(\eta)$ .

In actual diffractometry, however, the scan range and the size of the receiving slit would give a limit of integration of diffuse intensities and hence smaller values than the above would be measured, giving

$$I_D = \frac{C}{4} \varepsilon^2 N_1 N_2 N_3 |P - Q|^2 \quad (4)$$

where  $\varepsilon^2$  is the ratio of an observed intensity recorded through the receiving slit to the total intensity of the diffuse reflection. If the instrumental broadening is very small, the value of  $\varepsilon^2$  may be given approximately by

$$\begin{aligned} \varepsilon^2 &= \int_{k'-\Delta\eta}^{k'+\Delta\eta} [(1-x^2)/(1+x^2-2x \cos 2\pi\eta)] d\eta \\ &= (2/\pi) \arctan \left( \frac{1-x}{1+x} \tan \pi\Delta\eta \right). \end{aligned} \quad (5)$$

The integration limit  $\pm\Delta\eta$  (and hence the value of  $\varepsilon^2$ ) would depend not only on the above instrumental conditions but also on the direction of  $\mathbf{b}^*$  with respect to the scanning direction.

The structure factors for reflections with  $k$  even and odd are then given by  $P + Q$  and  $\varepsilon(P - Q)$  respectively, which give a modulated electron density distribution  $\rho(r)$  as

$$\rho(r) = \rho_o(r) + (\varepsilon - 1) \rho_{od}(r). \quad (6)$$

Here we tentatively assumed  $\varepsilon$  to be constant for all diffuse reflections;  $\rho_o(r) = \rho_{ev}(r) + \rho_{od}(r)$  shows the electron density distribution of the  $PQ$  cell;  $\rho_{ev}(r)$  and  $\rho_{od}(r)$  are electron densities obtained from  $(P + Q)$ 's and  $(P - Q)$ 's respectively (see Sakurai, 1958).

From equation (6) it can be seen that the modulated peaks on a Fourier map,  $\rho(r)$ , would be produced from the modulation term  $(\varepsilon - 1) \rho_{od}(r)$ , and further the most modulated peaks might be found at the positions where the maximum or minimum electron densities are found on  $\rho_{od}(r)$ . In our case, the ghost found at the Li(1) position may well be explained by the fact that this position corresponds to that of a deep negative pit for the Co atom on  $\rho_{od}(r)$ ; *i.e.* the peak density  $(\varepsilon - 1) \rho_{od}(r)$  of the Co atom is superposed on the peak of the Li(1) atom.

From the above result it may be concluded that the large peak density found at the Li(1) position is attributable to the superposition of a ghost due to truncation errors in the intensity measurements of diffuse reflections. To confirm this, we collected intensity data, under the same instrumental conditions, from the crystal used in this study, and calculated a Fourier synthesis using phases for the crystal used for

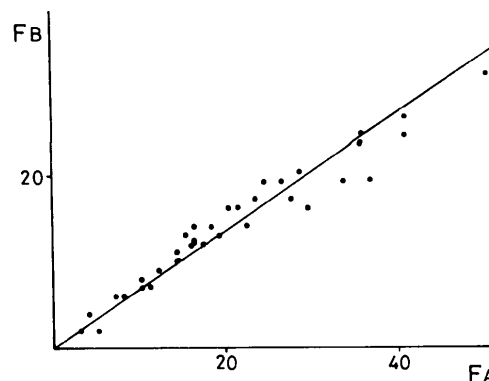


Fig. 3. Plot of structure amplitudes with  $h1l$  ( $F_A$ ) for the crystal used in this study vs the corresponding structure amplitudes ( $F_B$ ) for the crystal used for the structure determination.

the structure determination by YAST. As was expected, a very large peak density, which was as large as those of the O atoms, was observed at the Li(1) position. Fig. 3 shows a comparison of the structure amplitudes with  $h1l$  for the two crystals. The linearity found in Fig. 3 indicates that the value of  $\varepsilon$  may be taken to a first approximation as constant for all diffuse  $h1l$  reflections. Such a linearity was also found for reflections with  $hkl$  ( $k = 3, 5, 7, \dots$ ) though slightly steeper slopes were found as  $k$  increased.

On the basis of the above result, YAST (1979) obtained several sets of  $F_o$ 's by multiplying the original  $F_o$ 's ( $k$  odd) by a constant value of  $1/\varepsilon$  for  $\varepsilon > 0.8$  and carried out least-squares calculations for each set of  $F_o$ 's. A plausible value of  $\varepsilon = 0.92$  was then obtained on the assumption that the temperature factor for Li(1) is approximately equal to that for Li(2). An approximate value of  $\varepsilon$  for the 110 reflection from the crystal used in this study can then be estimated from the slope

of 0.67 of Fig. 3 to be  $\varepsilon = 0.92 \times 0.67 = 0.62$ . Substituting this value and  $\alpha = 0.045$  ( $x = -0.91$ ) into equation (5) gave  $\Delta\eta = 0.01$ . Using this value we have an approximate value of  $\alpha \approx 0.008$  for the crystal used for structure determination.

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## Structure of the Potassium Tantalum Fluoride Oxide $K_3Ta_4F_7O_8$

BY A. BOUKHARI, J. P. CHAMINADE, M. POUCHARD AND M. VLASSE

*Laboratoire de Chimie du Solide du CNRS, Université de Bordeaux I, 351 cours de la Libération, 33405 Talence CEDEX, France*

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#### Abstract

$K_3Ta_4F_7O_8$  crystallizes in space group  $Pmn2_1$  with  $a = 3.918$  (3),  $b = 18.072$  (7),  $c = 19.057$  (7) Å,  $Z = 4$ . The structure was refined to  $R = 0.083$ . The main structure is formed by  $TaX_6$  ( $X = O, F$ ) distorted octahedra sharing common corners. It can be described as an assembly of two-dimensional  $[Ta_4X_{15}]_n$  infinite blocks parallel to the (001) plane held together by the K atoms.

#### Introduction

Compounds with layer or tunnel structures may be particularly suitable for fast-ion transport, so far as they offer to the inserted ion a certain degree of freedom. This property is conditioned by the nature of the structural pathways and of the transporting ion (Pouchard & Hagenmuller, 1978).

Many structures derived from or related to the tungsten-bronze types are made up of a triangular motif of three  $BX_6$  octahedra sharing common corners ( $B_3X_{15}$ ). These basic blocks can be joined together by

common corners, in one plane, giving rise to complex structures having infinite tunnels normal to such sheets. The tunnels can be hosts to monovalent or divalent cations.

Many phases have been isolated in the study of the system  $A^I-B^V-O,F$  ( $A = Li, Na, K, Ag$ ;  $B = Nb, Ta$ ) (Vlasse, Chaminade & Pouchard, 1973, 1976; Chaminade, Vlasse, Pouchard & Hagenmuller, 1974; Vlasse, Chaminade, Massies & Pouchard, 1975; Vlasse, Chaminade, Saux & Pouchard, 1977). In particular, the study of the subsystem K-Ta-O-F has produced four new phases. The structures of  $K_6Ta_{6.5}F_{9.5}O_{14.5}$ ,  $K_2Ta_4F_4O_9$  and  $K_{12}Ta_{15.5}F_{18.5}O_{35.5}$  have been reported (Vlasse, Boukhari, Chaminade & Pouchard, 1979; Boukhari, Chaminade, Vlasse & Pouchard, 1979; Boukhari, Chaminade, Pouchard & Vlasse, 1979). The present report deals with the analysis of  $K_3Ta_4F_7O_8$ .

#### Experimental

Single crystals were obtained by reacting appropriate quantities of  $K_2TaF_7$ ,  $KTaO_3$  and  $Ta_2O_5$  in a sealed