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## A TECHNIQUE FOR USING TWINS IN CRYSTAL STRUCTURE REFINEMENT

R. L. FREED, *Department of Geology and Mineralogy,  
University of Oxford, England.*<sup>1</sup>

If the crystal structure of a compound is known and a twin must be used for refinement of the structure, then the twinning relation can be used to interpret the observed intensity values. The problem becomes the task of calculating the crystal-volume ratio, which may be defined as the ratio  $K = V_{\beta}/V_{\alpha}$  of the volume  $V_{\beta}$  of the smaller crystal to the volume  $V_{\alpha}$  of the larger crystal,  $0 < K < 1$ . If the twin produces two sets of reflections, each set self-consistent within its own indexing, then the crystal-volume ratio can be calculated by direct comparison of equivalent reflections from each set. If the two twinned crystals produce reflections that are superimposed on each other, then a least-squares solution can be employed as described below. This method has been used successfully (Freed and Peacor, 1967) for a case which yielded the value  $K = 0.07$ .

Let  $v_1, v_2, \dots, v_n$  be the volume fractions of the  $n$  constituent crystals in the twin, so that  $\sum_{i=1}^n v_i = 1$ . For a given reflection  $hkl$  the intensities will be  $v_1I, v_2I, \dots, v_nI$ , where  $I$  stands for  $I(hkl)$ , the intensity contributed by a volume equal to the total volume  $\sum v_i$  of the twin. In a two crystal twin, the fractions will be  $v$  and  $(1-v)$ , and the crystal-volume ratio can be expressed  $K = (1-v)/v$ .

<sup>1</sup> Present address: Department of Geology and Mineralogy, University of Michigan, Ann Arbor, Mich.

Calling, as above,  $\alpha$  and  $\beta$  the two crystals in the twin, an observed intensity,  $I$ , would be the sum of the intensity  $vI$  of the reflection from individual  $\alpha$ , and the intensity  $(1-v)I$  of the superimposed reflection from individual  $\beta$ . Then if  $X$  and  $x$  represent the indices of reflections superimposed by the twin law, and if we index the total intensity to correspond to the larger crystal, we have:

$$vI_X + (1-v)I_x = I_X \quad (1)$$

$$vI_x + (1-v)I_X = I_x \quad (2)$$

These equations may be combined to give:

$$vI_X = [(v^2)/(2v-1)]I_X - [v(1-v)/2v-1]I_x \quad (3)$$

where  $vI_X$  is the desired intensity value.

In order to simplify equation (3), we will define  $K_1 = (v^2)/(2v-1)$ , and  $K_2 = v(1-v)/(2v-1)$ . It should be noted at this point that  $K_2/K_1 = (1-v)/v$ , which is the crystal-volume ratio. Equation (3) can be written:

$$vI_X = K_1I_X - K_2I_x \quad (3a)$$

Least-squares techniques can be applied to equation (3a) as follows:

$$\gamma = K_1I_X - K_2I_x - vI_X$$

$$\Sigma\gamma^2 = \Sigma(K_1I_X - K_2I_x - vI_X)^2 = \text{minimum.} \quad (4)$$

Taking the partial derivatives of  $\Sigma\gamma^2$  with respect to  $K_1$  and  $K_2$  and setting the resulting expressions equal to zero gives:

$$K_1\Sigma I_X^2 - K_2\Sigma I_X I_x = \Sigma I_X v I_X \quad (5a)$$

$$K_1\Sigma I_X I_x - K_2\Sigma I_x^2 = \Sigma I_x v I_X \quad (5b)$$

Equations (5a) and (5b) may be solved for  $K_1$  and  $K_2$ . Therefore, a value for the crystal-volume ratio,  $K = K_2/K_1$ , can be obtained in terms of the original intensity values and approximate  $vI_X$  values initially obtained from structure factor calculations.

The procedure during refinement is to start with the original observed intensity values and approximate values for the  $vI_X$  terms, and use the least-squares equations to calculate  $K_1$  and  $K_2$ . Equation (3a) is then used to find new  $vI_X$  values which are used in the structure refinement. The structure is refined, a list of calculated structure factors is generated, and these calculated values are then used as new approximate  $vI_X$  values. Care should be taken to ensure that the approximate  $vI_X$  values used in each cycle of refinement are scaled to the same level. This procedure results in two additional variables being refined ( $K_1$  and  $K_2$ ), and this must

be considered when using a small number of reflections, and also in the interpretation of the residual,  $R$ .

Some other practical considerations are involved in the use of this method. If the twinning can be optically observed, then it may be impossible to apply an adequate absorption correction. If the twinning cannot be observed optically, then the twin "domains" are small, which indicates that an acceptable absorption correction can be applied by treating the twin as a single crystal. The refinement of values of  $K$  other than 0.07 has not been tested, and it is not known how difficult it would be to refine structures as  $K$  approaches 1.0. Errors in  $K_1$  and  $K_2$  will affect the "Wilson" scale factor, and, therefore, also the calculated temperature factors. Ideally, errors in  $K_1$  and  $K_2$  should be taken into consideration when errors in final parameters are interpreted.

Keffer *et al.*, (1967) used a twin for refinement of the crystal structure of low-temperature lithium phosphate. Their approach was similar to the method outlined above in that unequal volume fractions of two crystals were present in the twin. However, because they were dealing with twinning on a unit-cell scale, there were coherent phase relations between the diffracted beams from the two twinned crystals; therefore, amplitudes rather than intensities were added. (See also Clark *et al.*, 1966.)

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