

IF YOUR ONLY SINGLE CRYSTAL IS NOT REALLY SINGLE

L. W. FINGER

*Geophysical Laboratory and Center for High-Pressure Research, 5251 Broad Branch Road,
N.W. Washington, DC 20015-1305 USA*

A method for deconvolution of overlapping peaks from twinned single crystals has been developed. Each contributor is composed of a doublet corresponding to the $K\alpha_1$ and $K\alpha_2$ wavelengths. By least-squares refinement of a highly-constrained representation of this doublet, the intensity due only to the main crystal can be extracted. This method has been applied to one of the recently discovered high-temperature superconductor materials.

Introduction

With modern developments in high-brightness sources, fast and accurate single-crystal diffractometers, and software for solution of crystal structures, the determination of the structure of a given material depends upon finding a single crystal that is "good" enough. In many cases, the search is nontrivial. For example, when materials are synthesized at nonambient conditions, it is possible for phase transitions to occur upon the temperature quench and/or pressure release, which may result in twinning. Two such systems currently subject to considerable crystallographic research include high- T_c superconductors and high-pressure minerals. Even if untwinned crystals can be selected, the fine grain size of many such experiments make it difficult to select only one crystal. As a result, the diffraction experiment may include several smaller fragments.

This report describes a technique to extract high-quality data from the diffraction data, even though the sample is twinned, or composed of several individuals.

Twinning

Twinning of minerals has been extensively studied [1]. As the above authors state "Composite crystals of a single substance, in which the individual parts are related to one another in a definite crystallographic manner, are known as *twinned crystals* [original emphasis]." Twinned crystals can originate during crystal growth where the alternate arrangement contributes only a small increase in the total energy over that of the untwinned form. Alternatively, twins can form dur-

ing transformations from a high symmetry to a lower one. A classic example is when β -quartz (SiO_2) with space group $P6_222$ or $P6_422$ transforms to α -quartz with space group $P3_121$ or $P3_221$. Pairs of space groups are listed above as each can exist in either of two enantiomorphs, a right or left-handed form. Although left-handed β -quartz always transforms to the left-handed α -form, the lower symmetry form can nucleate in either of two possible arrangements, related by the two-fold about the c-axis that is present in the β form, but absent in α -quartz. This twin mechanism is called the Dauphine law. The volumes of the twinned individuals will depend upon nucleation and growth kinetics of the transformation. Another form of twinning, the Brazil law, is formed from intergrowths of individuals with opposite handedness. Unlike the Dauphine law, twins formed by the Brazil law can be visible under crossed polarizers because they rotate the plane of polarization in opposite directions.

Both twin laws described above yield composites in which there is perfect overlap of the reciprocal lattices of the individuals, with no twinning information contained in the shapes of the diffraction maxima. Only the intensities of the diffraction data are affected. This type of twinning can occur in any (merohedral) crystal class that has fewer symmetry elements than the Laue group, which has the maximum symmetry for the lattice geometry.

The intensities measured in the presence of merohedral twinning can be corrected because the intensities from the individuals are additive. For the general case, the measured intensities I_m are represented by

$$I_m = \sum_n a_n I_n \quad (1)$$

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subject to the constraint that $\sum_n a_n = 1$, where a_n is the volume fraction of the n 'th individual, and I_n is its intensity. If the effects of self absorption are ignored, the squares of structure factors can be substituted for intensities and the independent values of the volume fractions can be refined. A standard least-squares program can be used if it is modified to generate suitable Miller indices for the extra individuals. One such computer program that has been modified to treat such diffraction data is RFINE90, a modified version of RFINE4 [2]. This program has been used to refine data from α -quartz with Dauphine twinning [3], where the crystal included 5% of a twin component.

If the universe of multiple crystals were divided into a continuum, such merohedral twinning is clearly one extreme. Another extreme occurs when two, or more, crystals happen to be stuck together with no obvious crystallographic relationship. This case causes relatively few problems in data analysis because the few diffraction intensities that suffer from overlap can be rejected from the data set. Again there could be problems with an absorption correction; however, it is not, in general, difficult to identify the intensity arising from the unwanted individual.

Pseudo-merohedry

Cases intermediate between the two extremes described above may arise from either twinning or epitaxy. For twinned crystals, any pseudo-symmetry operation of the lattice may form the twin operator. A well-known example occurs for the high- T_c superconductor with composition $YBa_2Cu_3O_{6+\delta}$, which is orthorhombic with a and b nearly equal in length. At high temperatures, the true symmetry is tetragonal, but upon cooling and inversion to the orthorhombic, low-temperature form, two different orientations may occur. Nucleation and growth kinetics will determine the relative amounts of the two forms.

Another case of pseudomerohedral twinning is seen for $HgBa_2Ca_2Cu_3O_{8+\delta}$ [4]. Although the material is tetragonal at room temperature, the best crystal that was available showed multiple individuals with varying degrees of splitting corresponding to a 120-degree rotation about [113]. Some diffraction profiles were free of interference (Fig. 1a), and others could be separated (Fig. 1 b). In some cases, however, this extra intensity could not be eliminated in the calculation of integrated

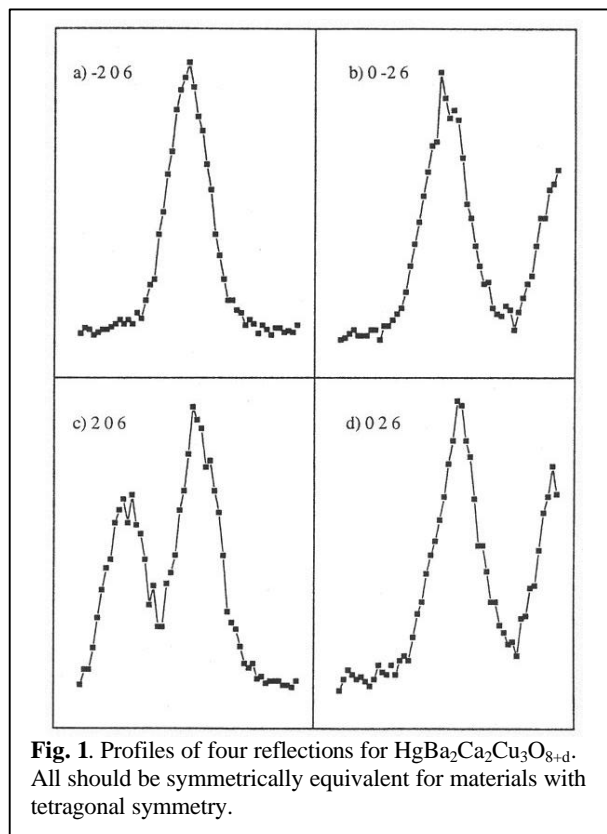


Fig. 1. Profiles of four reflections for $HgBa_2Ca_2Cu_3O_{8+d}$. All should be symmetrically equivalent for materials with tetragonal symmetry.

intensities. Accordingly, attempts were made to develop a modification to the least-squares program that would account for extra intensity from pseudo-merohedral operations that would be collected in the diffraction experiment. All such attempts failed and no algorithm could be devised that would predict what fraction of the extra components could not be removed in the diffraction experiment. I decided, therefore, to use the measured step profiles to isolate the intensity from the primary crystal, thereby eliminating interference before starting any least-squares process. If such a technique could work, it would have the additional benefit that the structure need not be known to produce a set of intensities nearly free of the effects of twinning.

Peak Profile

The profile of the 330 diffraction peak for our ruby alignment crystal ($2\theta=53.11$ degrees), obtained by rotating the crystal about the θ -axis, is shown in Fig. 2. These data were collected on a Rigaku AFC5R diffractometer with a β -filter rather than a monochromator. The envelope is seen to be reasonably well represented by a super-

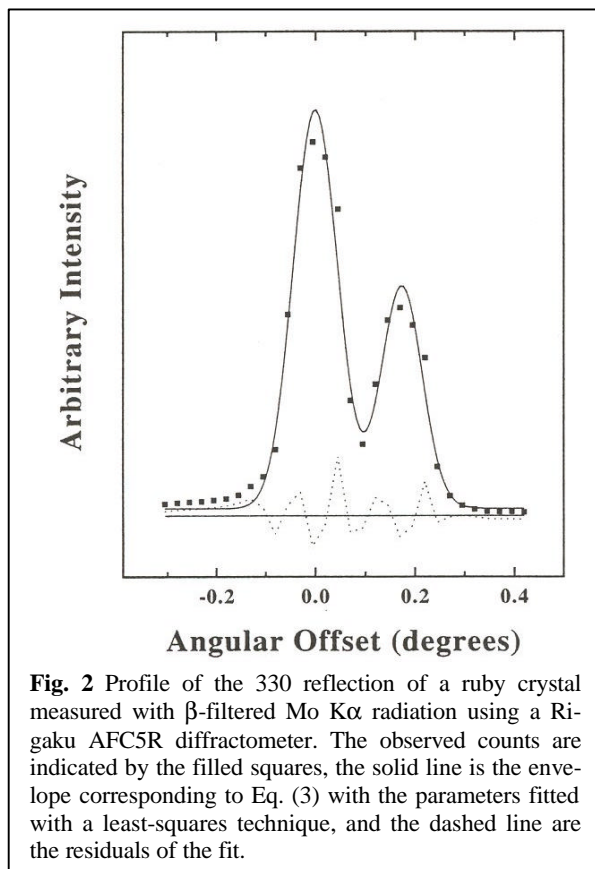


Fig. 2 Profile of the 330 reflection of a ruby crystal measured with β -filtered Mo $K\alpha$ radiation using a Rigaku AFC5R diffractometer. The observed counts are indicated by the filled squares, the solid line is the envelope corresponding to Eq. (3) with the parameters fitted with a least-squares technique, and the dashed line are the residuals of the fit.

position of two Gaussian peaks, one for each member of the $K\alpha$ doublet. The most general form of such a profile is (2):

$$I(\mathbf{q}) = \frac{I_{K\alpha 1}}{\Gamma_1} e^{-(\mathbf{q}-\mathbf{q}_{K\alpha 1})^2/\Gamma_1^2} + \frac{I_{K\alpha 2}}{\Gamma_2} e^{-(\mathbf{q}-\mathbf{q}_{K\alpha 2})^2/\Gamma_2^2} + B$$

where $I_{K\alpha 1}$ and $I_{K\alpha 2}$ are the integrated intensities of the two components, Γ_1 and Γ_2 are the full-widths at half maximum (FWHM), θ is the position at which the profile is evaluated, and B is the background.

For peaks as sharp as in this example, there would be no difficulty in fitting two unconstrained Gaussians; however, at lower 2θ the peak separation is reduced. If, in addition, the peaks are broader, the least-squares refinement of the Gaussian parameters will be unstable. Accordingly, the physics of the X-ray production can be used to simplify the problem. The intrinsic widths of $K\alpha 1$ and $K\alpha 2$ are not significantly different; therefore, a single FWHM, represented by Γ , can be used. Secondly, the intensities of the two peaks should have a ratio of 2:1. For the final simplification,

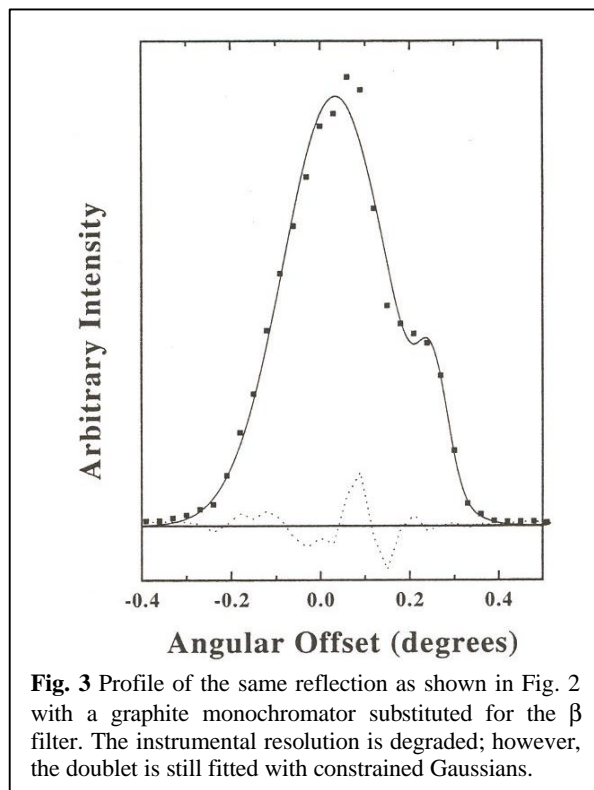


Fig. 3 Profile of the same reflection as shown in Fig. 2 with a graphite monochromator substituted for the β filter. The instrumental resolution is degraded; however, the doublet is still fitted with constrained Gaussians.

Bragg's law can be differentiated to show that the angular separation between the $K\alpha 1$ and $K\alpha 2$ peaks is given by $\Delta\theta = \Delta\lambda/\lambda \tan \theta$ in radians. Therefore, $\theta_{K\alpha 2}$ is replaced by $\theta_{K\alpha 1} + 180\Delta\lambda/(\pi\lambda) \tan \theta_{K\alpha 1}$. The peak can be fitted by

$$I(\mathbf{q}) = \frac{I_{K\alpha 1}}{\Gamma} \left[e^{-(\mathbf{q}-\mathbf{q}_{K\alpha 1})^2/\Gamma^2} + 1/2 e^{-(\mathbf{q}-\mathbf{q}_{K\alpha 1}-180\Delta\lambda/(\pi\lambda) \tan \theta_{K\alpha 1})^2/\Gamma^2} \right] + B \quad (3)$$

The need for the constraints employed in Eq. 3 is obvious in Fig. 3, which shows the profile of the same reflection and crystal when a graphite monochromator is employed. The reflection width is increased by the poor energy resolution of the graphite; however, the constrained doublets can be fitted.

Integrated Intensities

Although it is possible to fit reflection profiles such as those found in Figs. 2 and 3 with relatively small residuals, the integrated intensities obtained by such a process must be tested to prove that a successful refinement of the crystal structure will result from the application of such a procedure. Accordingly, a complete set of intensity data were extracted from the data set correspond-

Table 1 Refined parameters for ruby alignment crystal.

Parameter	Lehman-Larson method	Gaussian peak fit
R	0.014	0.013
wR	0.012	0.017
Extinction	3.0(2)	3.2(3)
z, Al	0.35218(3)	0.35221(3)
x, O	0.6939(1)	0.6939(2)
β_{11} , Al	0.0050(3)	0.0052(4)
β_{33} , Al	0.00041(3)	0.00048(4)
β_{11} , O	0.0059(3)	0.0063(4)
β_{22} , O	0.0060(4)	0.0064(5)
β_{33} , O	0.00051(4)	0.00056(5)
β_{13} , O	0.00013(3)	0.00015(4)

Notes: Space Group $R\bar{3}c$, $a=4.759(1)$ Å, $c=12.992(2)$ Å, Al at (0,0,z), O at (x,0,1/4). All intensities to $\sin \theta/\lambda = 0.67$ measured on a Rigaku AFC5R diffractometer with a graphite incident-beam monochromator.

ing to Fig. 3. Two methods were employed: (1) a modified Lehman-Larsen technique [5, 6], and (2) the fitted Gaussian method of Eq. 3.

The results of least-squares refinement of the two data sets are presented in Table 1. The conventional R factor for the Gaussian fitted data is slightly better; however, the weighted R is somewhat worse. Clearly, the relative weights of the two data sets are different. Despite this discrepancy, the refined parameters are identical within two standard deviations. It can be concluded, therefore, that integrated intensities produced by the new technique are comparable with those obtained by more conventional means.

The constrained Gaussian fitting procedure described here was used to extract integrated intensities from the data set for $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ shown in Fig. 1. For those scans with multiple peaks, the envelope nearest the center of the scan was chosen as the intensity belonging to the main crystal. A number of profiles were found to include extra contributions that were not resolved, as evidenced by a larger than expected FWHM. Such peaks were not included in the final data set. The final refinement of the resulting data converged to $wR=0.072$ and $R=0.094$. Although such results are not particularly good, it must be remembered that this material is very highly absorbing ($\mu_t=325\text{cm}^{-1}$); therefore, absorption corrections are difficult, particularly for a twinned crystal. Without access to the deconvolution technique, we could not have done this analysis.

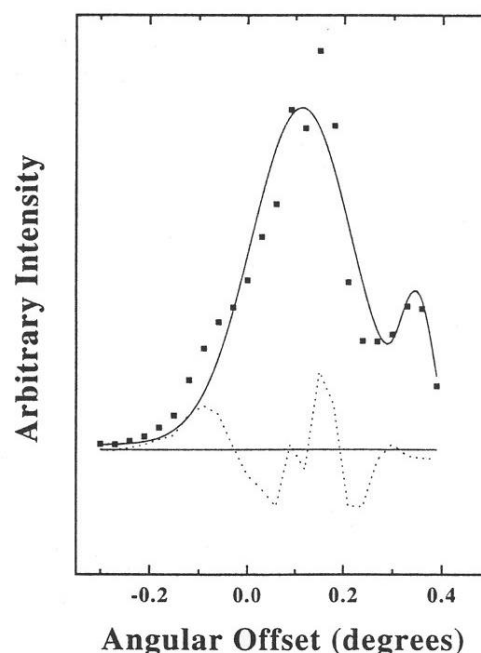


Fig. 4 Profile of the same reflection as shown in Figs. 2 and 3 with an extra shoulder on the low-angle side of the doublet is produced by a misalignment of the graphite crystal. If a constrained fit is to be used to extract diffraction intensities, this type of misalignment must be corrected.

Proper alignment of the single-crystal diffractometer is important for the measurement of accurate intensities; however, the deconvolution procedure adds an additional requirement. Fig. 4 displays an envelope for the ruby reflection shown in Fig. 3 obtained with a slight misalignment of the monochromator. This error causes an extra shoulder on the low-angle side of the envelope, which cannot be fitted by Eq. 3 as can be seen by the relatively large residuals.

Conclusions

With the use of the peak deconvolution method presented here, integrated intensities suitable for structural refinement can be extracted from many crystal fragments that cannot be treated by conventional intensity integration.

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