

# Application of Synchrotron Radiation Laue Diffraction to Small Single Crystals of a Mineral – Structure Determination and Identification

Benson M. Kariuki and Marjorie M. Harding

Chemistry Department, University of Liverpool, Liverpool L69 3BX, UK

(Received 9 March 1995; accepted 21 April 1995)

The potential of synchrotron radiation Laue diffraction patterns for structure determination and for identification of small single crystallites is illustrated. Diffraction patterns were recorded for several crystallites,  $\leq 20 \mu\text{m}$  in all dimensions, with the intention of determining an unknown mineral structure. They were the largest particles in the sample. They appeared to represent at least two different phases, but eventually it became clear that neither corresponded to the unknown phase. However, it has been possible to show that both identification and structure determination are practicable from Laue diffraction patterns of crystallites of this size. For one crystallite the diffraction patterns were used to derive unit-cell dimensions and from these the crystallite could be identified as either  $\text{PbCO}_3$ , cerussite, or  $\text{SrCO}_3$ , strontianite. Using intensity measurements it could be shown to be  $\text{PbCO}_3$ . Identification could be similarly achieved for many other small single crystallites, and the procedure is described. For another crystallite, a complete structure determination was carried out and it was then recognized as malachite,  $\text{Cu}_2(\text{OH})_2\text{CO}_3$ . The structure found is in very good agreement with that previously determined by Zigan, Joswig, Schuster & Mason [*Z. Kristallogr.* (1977), **145**, 412–416].

**Keywords:** small crystals; mineral structure; Laue diffraction.

## 1. Introduction

Synchrotron radiation Laue diffraction has allowed us to record diffraction patterns and obtain structural information for two small single crystallites in a mineral sample, a mixed zinc, copper hydroxycarbonate. Our experiments were originally performed in order to determine the structure of a mineral phase, rosasite, for which the only previously available information was from X-ray powder diffraction data (Roberts, Jambor & Grice, 1986). After we had recorded the Laue diffraction patterns and interpreted them it became clear that neither of the crystallites we had selected corresponded to rosasite. For one (*A* below) unit-cell dimensions, or rather axial ratios, were accurately derived, and then the crystal could be identified as one of two possible carbonate minerals, by using a database of unit-cell information. For the other (*B*), the structure was completely determined from the Laue diffraction data, but the structure found was recognized as one already known. The dimensions of the crystallites were all  $< 20 \mu\text{m}$ . Synchrotron radiation Laue diffraction could be used for any small crystal of moderate quality, for either structure determination or partial identification, but could be of particular value in cases where there was neither sufficient material for X-ray powder diffraction, nor crystals of sufficient size for conventional single-crystal methods.

The method that would be used for complete crystal identification is outlined below. Most of the steps are also relevant for structure determination.

## 2. Method for crystallite identification

### 2.1. Recording the Laue diffraction patterns

The Laue diffraction patterns are currently recorded on film or image plate. Patterns from one crystal in several different orientations are required, for example at a series of angles around a spindle (see Helliwell *et al.*, 1989). If the crystal is very small, precautions need to be taken to reduce the background scattering so that sufficient diffraction spots can be identified; the crystal is mounted on a very fine glass fibre (*e.g.* glass wool, *ca*  $10 \mu\text{m}$  thick), the collimator-to-crystal and crystal-to-backstop distances should be very short, *e.g.*  $\leq 5 \text{ mm}$  each, to reduce the beam path length in air (which is often responsible for much of the background), and long-wavelength incident radiation (*e.g.*  $> 1 \text{ \AA}$ ) should be removed by an attenuator such as aluminium.

### 2.2. Determining a unit cell

Each Laue diffraction pattern is digitized and displayed as a gnomonic projection, from which may be derived the unit-cell edges of the crystal on a relative scale, the unit-cell angles and the crystal orientation (Carr, Cruickshank & Harding, 1992); the relevant programs are now incorporated in the *Daresbury Laue Software Suite* (Campbell, 1993). The final step in this stage is refinement of the unit-cell and orientation parameters with the program *LAUEGEN* (also in the *Daresbury Laue Software Suite*, Campbell, 1993) to match the predicted and observed positions of 100 or more diffraction spots on each pattern. With reasonable diffrac-

tion patterns the axial ratios obtained should be accurate to *ca* 0.5%, or possibly better. Some simplifications or short cuts may be possible: when the unit cell and orientation have been found for one pattern, it is easy to test whether the other patterns can be matched with the same cell and appropriately modified spindle angles; occasionally it is possible to find an orientation and axial ratios merely by trial and error and refinement in *LAUEGEN* (without using the gnomonic projection).

There are good tests by which to judge the correctness of the solution found. The root-mean-square displacement of observed from predicted spot positions should be small on each pattern; a value  $\leq 0.06$  mm should be achievable with good-quality crystals. A visual check is needed to make sure all spots are being predicted, not just a subset, and that a high proportion of the predicted spots are observed; without this precaution the unit cell chosen could be a multiple or submultiple of the true one. The axial ratios and unit-cell angles refined independently with the different diffraction patterns in the series must be in agreement with each other, and with the known differences in spindle angles.

### 2.3. Determination of the unit cell on an absolute scale

Determination of the unit cell requires that some of the Laue diffraction patterns be recorded with a suitable attenuator in the incident beam, *e.g.* palladium, 0.1 mm, to make the minimum wavelength present a sharp and identifiable limit (Carr, Dodd & Harding, 1993). Without this experimental information the absolute scale can still be estimated to within 10–20%, using the known characteristics of the beamline, and this may be sufficient to identify the crystal.

### 2.4. Identification

Identification can then be made with *CDIF* in the EPSRC Chemical Database Service or an equivalent database. *CDIF* currently contains nearly 200 000 entries. It uses the unit-cell dimensions, together with an estimate of (a) their relative accuracy, and (b) their absolute accuracy, and it may find one or more compounds which satisfy the criteria.

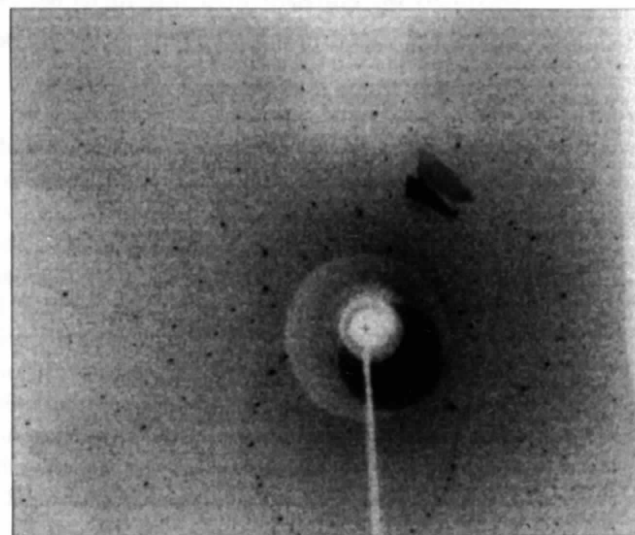
### 2.5. Intensity measurements

Intensity measurements, *i.e.* integration of spot intensities at the predicted positions, can be carried out on the Laue diffraction patterns using the *Daresbury Laue Software Suite* (Campbell, 1993), to give a set of indexed reflection intensities. Such intensity measurements for a small crystal of an organometallic compound are described in more detail by Dodd, Hao, Harding & Prince (1994). Structure-factor calculation can then show whether these are consistent with the proposed compound.

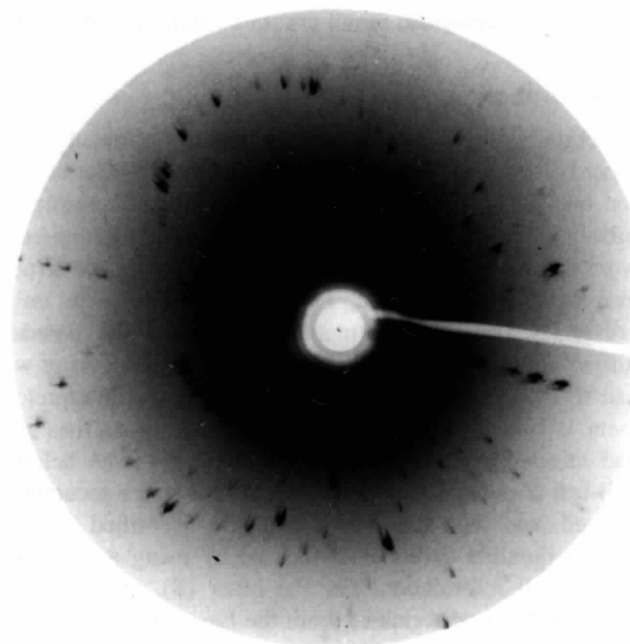
## 3. Application

Eleven crystallites from the sample of rosasite (supplied by Dr G. Cressey, Natural History Museum, London) were

selected and mounted with the intention of finding one which gave Laue diffraction patterns good enough for structure determination. They were the largest crystallites in the sample, but none was more than 20  $\mu\text{m}$  in any dimension. The Laue diffraction patterns of four crystallites had very similar characteristics (spot size, sharpness,



(a)



(b)

### Figure 1

(a) Laue diffraction pattern recorded on an image plate for crystallite A, identified as  $\text{PbCO}_3$ . Crystal dimensions  $20 \times 20 \times 5 \mu\text{m}$ ; other experimental details are given in the text. (The dark shadows are the result of unintended scattered radiation.) (b) Laue diffraction pattern recorded on film for crystallite B, whose structure is shown here to correspond to that of malachite,  $\text{Cu}_2(\text{OH})_2\text{CO}_3$ . Crystal dimensions  $20 \times 20 \times 10 \mu\text{m}$ ; other experimental details are given in the text. Diffraction patterns recorded in other orientations for this crystallite appeared even poorer with very streaked spots.

**Table 1**  
Unit-cell refinement for unknown crystal *A* and identification.

Spindle angle (°)	20	100	60	50	0	90
Number of spots used in refinement	182	215	194	207	180	171
R.m.s. displacement of predicted from observed positions (mm)	0.059	0.056	0.062	0.063	0.049	0.057
Relative <i>b</i> (Å)	9.70	9.70	9.69	9.73	9.69	9.69
Relative <i>c</i> (Å)	7.01	7.01	7.00	7.00	7.01	7.01
Estimated $\lambda_{\min}$ (Å)	0.36	0.36	0.30	0.32	0.30	0.32
Hence ( $\alpha = \beta = \gamma = 90^\circ$ )		<i>a</i>	<i>b</i>	<i>c</i>		
Mean value from six Laue images, on arbitrary scale e.s.d		5.91	9.70	7.01		
Mean value from Laue images scaled by factor $\lambda_{\min}(\text{true})/\lambda_{\min}(\text{observed}) (= 0.25/0.30)$ with estimated uncertainty 10–20% (Å)		4.925	8.083	5.842		
PbCO <sub>3</sub> , cerussite (Chevrier <i>et al.</i> , 1992) (Å)		5.179 (1)	8.492(3)	6.141 (2)		
ratio Laue/literature		0.951	0.952	0.951		
SrCO <sub>3</sub> , strontianite (Jarosch & Heger, 1988) (Å)		5.1039 (3)	8.4022 (4)	6.0220 (4)		
ratio Laue/literature		0.965	0.970	0.962		

The program *LAUEGEN* was used to refine the relative values of *b* and *c*, together with crystal orientation parameters. *a* was held constant at 5.91 Å.  $\alpha$ ,  $\beta$  and  $\gamma$  were also allowed to vary, but they refined to within 0.04° of 90°.  $d_{\min}$  and  $\lambda_{\min}$  were estimated to match the observed pattern.

distribution); one of these, for crystallite *A*, is shown in Fig. 1(a). It is probable that these four crystallites all represent one compound. Another, crystallite *B*, gave the pattern in Fig. 1(b) which appears to correspond to a completely different phase, and a much more poorly ordered crystal. The remainder gave patterns which were even poorer than *B*, and it was concluded, though possibly not correctly, that these were the same phase as *B*. From its unit cell, *A* could be identified as either PbCO<sub>3</sub>, cerussite (Chevrier *et al.*, 1992), or SrCO<sub>3</sub>, strontianite (Jarosch & Heger, 1988). For *B*, the structure was completely determined, but then recognized as that of malachite, Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> (Zigan, Joswig, Schuster & Mason, 1977). In neither case were additional Laue patterns recorded with a Pd attenuator in the incident beam for absolute cell determination; it had been assumed that it would be possible to establish the absolute scale of the cell of the unknown crystal using the powder diffraction pattern of rosasite.

### 3.1. Experimental

Laue diffraction patterns were recorded on SRS wiggler beamline, station 9.7, at Daresbury Laboratory, with a modified Huber goniometer, 0.2 mm collimator. For crystallite *A* the patterns were recorded on Molecular Dynamics image plates, crystal-to-plate distance 78 mm, exposure time 6 s; attenuators 0.2 mm Al plus 0.038 mm Cu in the incident beam were used; the SRS was running at 2 GeV, 185 mA. For crystallite *B* a 0.2 mm Al attenuator in the incident beam was used, the SRS was running at 104 mA; patterns were recorded on five film packs of six films each, separated by additional films as spacers, exposure time 99 s, crystal-to-film distance 62 mm, relative spindle angles 0, 20, 35, 55 and 70°; other details the same as *A*. (Image plates should be more convenient for data processing than film packs, and although they were recorded for *B* the software for image plates was not adequately adapted and tested at the time the films were processed.)

### 3.2. Crystallite *A* data processing

The image plates were scanned within 2 h of exposure, on a Molecular Dynamics scanner, raster size 88 µm; the useful area of the image plate was 186 × 174 mm. Trial-and-error indexing of the patterns was successful. Refinement for each image independently changed the cell substantially and the agreement of observed and predicted spot positions improved greatly. The parameters refined included crystal orientation angles, crystal-to-film distance, two unit-cell edges (the third must be held constant), and the usual camera constants. A spatial distortion correction was required to allow for distortion resulting from the mechanics of the scanner movement (Campbell, Harding & Kariuki, 1995). The results are shown in Table 1. Visual comparison of observed and predicted patterns indicated excellent agreement. The agreement of the results of six independent refinements and the low root-mean-square deviations for the prediction of spot positions provide convincing evidence that the indexing and the unit cell (on an arbitrary scale) are correct. The absolute scale of the unit cell was estimated roughly using the known characteristic of the beamline,  $\lambda_{\min} \simeq 0.25$  Å. A search of the database *CDIF* (EPSRC Chemical Database Service) could then be made, selecting the orthorhombic system, using *a*, *b* and *c* deduced, and specifying relative errors in cell dimensions  $\leq 0.5\%$ , absolute errors  $\leq 20\%$ . This found only the minerals cerussite, PbCO<sub>3</sub>, and strontianite, SrCO<sub>3</sub>, and one organic phase; data are given in Table 1.

Distinction between PbCO<sub>3</sub> and SrCO<sub>3</sub> was sought by completing the intensity measurements and comparison with those expected for the known structures of PbCO<sub>3</sub> and SrCO<sub>3</sub>. It was necessary to use an early version of the software concerned with image-plate processing and the intensity measurements are therefore not quite as good as the Laue method is capable of. In spot prediction for integration the soft limits were taken as  $\lambda_{\min} = 0.26$ ,  $\lambda_{\max} = 2.5$  and  $d_{\min} = 0.48$  Å. *INTLAUE*, with profile fitting,

for integration gave 600–770 good spot measurements per film pack. Wavelength normalization and merging of the images with *LAUENORM*, using the wavelength range 0.34–0.80 Å, gave 1504 single reflections with  $R_{\text{merge}} = 0.094$  (*INTLAUE* and *LAUENORM* are in the *Daresbury Laue Software Suite*, Campbell, 1993). Using the coordinates and atomic displacement parameters of Chevrier *et al.* (1992) for  $\text{PbCO}_3$  as a starting model, refinement (*SHELXL*; Sheldrick, 1993) with this intensity data gave  $R = 0.11$  for 555 reflections (now merged as orthorhombic) with  $F > 4\sigma(F)$ . Similar refinement with Sr in place of Pb gave  $R = 0.16$  for the same reflections. The agreement is much better for  $\text{PbCO}_3$  than for  $\text{SrCO}_3$ .

### 3.3. Crystallite B data processing

The films were digitized (50 µm raster) and then indexed by trial and error, followed by refinement with *LAUEGEN*. The root-mean-square deviation of predicted from observed positions was 0.04 to 0.12 on *A* films, which we considered acceptable on account of the very poorly shaped spots (Fig. 1*b*). The absolute scale of the unit cell was chosen to make  $\lambda_{\text{min}} = 0.25$  Å.

In spot prediction for integration, the soft limits were estimated visually to be  $\lambda_{\text{min}} = 0.25$ ,  $\lambda_{\text{max}} = 2.5$ ,  $d_{\text{min}} = 0.9$  Å. A new integration routine, *SAINTE* (Hao, Harding & Campbell, 1995), which imposed a simple elliptical profile (spot length 2–2.5 mm, width 0.7–0.8 mm), was used for spot integration and, after merging of the films within each pack, gave 350–400 measured spots per film pack. Wavelength normalization and merging of the five film packs with the program *LAUENORM* used wavelengths in the ranges 0.30–0.48 and 0.49–0.93 Å and gave 740 (single) reflections with merging  $R = 0.17$  ( $R_1$  of the program); 410 of these had  $I > 1.5\sigma(I)$  and merging  $R = 0.15$ . Inevitably, the spot dimensions used in integration were a compromise between those large enough to cover the larger spots and those small enough to allow smaller close spots in dense regions like  $hk0$  to be separately measured. The accuracy of the integrated intensities was therefore limited.

### 3.4. Crystallite B structure solution

No assumptions were made about crystal symmetry in the above integration procedures. Inspection of the reflection intensities in a weighted reciprocal lattice, bearing in mind the limitation in the accuracy of the intensity measurements, indicated  $2/m$  diffraction symmetry. (It also showed that a simpler primitive cell could have been chosen, and the data were reindexed.) There were not sufficient  $h0l$  or  $0k0$  data to make deductions about glide planes or screw axes, so in the initial structure solution no assumptions were made about crystal symmetry. A solution was found from a Patterson function followed by a series of electron-density maps. It could be seen to conform to space group  $P2_1/a$ , and it could be refined with *SHELXL* (Sheldrick, 1993) to  $R = 0.12$  for 153 unique reflections with  $F > 4\sigma(F)$ ,  $R = 0.15$  for all reflections. At this stage

**Table 2**

Crystal data and structure refinement for crystallite *B*, and comparison with results for malachite (Zigan, Joswig, Schuster & Mason, 1977).

(a) Crystal data comparison

	Crystallite <i>B</i>	Malachite
Formula assumed	(Cu,Zn) <sub>2</sub> (OH) <sub>2</sub> CO <sub>3</sub>	Cu <sub>2</sub> (OH) <sub>2</sub> CO <sub>3</sub>
Space group	$P2_1/a$	$P2_1/a$
<i>a</i> (Å)	9.69 (10)	9.502
<i>b</i> (Å)	12.30 (12)	11.974
<i>c</i> (Å)	3.29 (7)	3.240
$\beta$ (°)	97.6 (7)	98.75
Crystal volume (mm <sup>3</sup> )	$4 \times 10^{-6}$	0.3

(b) Additional experimental data and information on refinement

Absorption coefficient	1.08 mm <sup>-1</sup> at $\lambda = 0.30$ Å 7.42 mm <sup>-1</sup> at $\lambda = 0.60$ Å 22.3 mm <sup>-1</sup> at $\lambda = 0.90$ Å
$\theta$ range for data collection (°)	7–24
Index ranges	$-10 \leq h \leq 9$ , $-13 \leq k \leq 13$ , $0 \leq l \leq 3$
Independent reflections	255 [ $R(\text{int}) = 0.20$ ] 153 with $I > 2\sigma(I)$
Refinement method	Full-matrix least squares on $F^2$
Number of parameters	43
Goodness-of-fit on $F^2$	0.792
Final R indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.12$ , $wR_2 = 0.30$
R indices (all data)	$R_1 = 0.145$ , $wR_2 = 0.32$
Largest difference peak and hole (e Å <sup>-3</sup> )	1.2 and -1.4

(c) Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{Å}^2 \times 10^3$ ) found for crystallite *B* are given on the first line of each pair. The coordinates are compared with those determined by Zigan, Joswig, Schuster & Mason (1977) in an accurate neutron diffraction study of malachite (second line of each pair). The coordinate origin has been moved (by 0.5,0.5,0.5) and the atom numbering adjusted to match our coordinates.  $U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor. The metal atoms are named Cu, but in our refinement the scattering factor corresponded to 0.5Cu + 0.5Zn.

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
Cu(1)	7302 (7)	8935 (3)	8867 (20)	31 (2)
Cu(1)	73242 (6)	89331 (5)	8880 (2)	
Cu(2)	9980 (6)	7882 (4)	3927 (16)	29 (2)
Cu(2)	99814 (6)	78793 (5)	3925 (2)	
O(1)	591 (4)	851 (2)	405 (9)	35 (7)
O(1)	59403 (10)	85155 (7)	4191 (3)	
O(2)	872 (5)	916 (3)	357 (11)	39 (8)
O(2)	87725 (9)	91615 (8)	3598 (3)	
O(3)	834 (3)	739 (2)	961 (8)	17 (5)
O(3)	83325 (8)	73541 (7)	9500 (3)	
O(4)	826 (5)	558 (3)	1160 (10)	40 (7)
O(4)	83412 (9)	55622 (7)	11308 (3)	
O(5)	629 (4)	639 (2)	856 (9)	31 (7)
O(5)	63150 (9)	63646 (7)	8417 (3)	
C(1)	765 (5)	643 (3)	983 (8)	14 (8)
C(1)	76622 (7)	64075 (6)	9727 (2)	

it was recognized as the structure of malachite, and our results were compared with the single-crystal results of Zigan, Joswig, Schuster & Mason (1977), a very accurate neutron diffraction study which gave  $R = 0.021$  for 635 reflection intensities. Table 2 gives some details of the structure determination and refinement, and its comparison

with malachite. All parameters, observed and calculated structure factors, and slightly fuller details of the structure determination from the Laue data have been deposited.\*

#### 4. Results and discussion

On the basis of axial ratios alone, the identity of crystallite A can be narrowed to two possibilities, SrCO<sub>3</sub> or PbCO<sub>3</sub>, which are isostructural. The axial ratios of these two compounds differ by less than 0.5%, the absolute values of the unit-cell edges by less than 2% (see Table 1). Whether the crystallite is SrCO<sub>3</sub> or PbCO<sub>3</sub>, the absolute error in cell dimensions is no greater than 5%. The agreement is better for PbCO<sub>3</sub>, with a discrepancy of only 0.1% in the axial ratios, but SrCO<sub>3</sub>, with a discrepancy of 0.8%, must be acknowledged to be a possibility. Distinction between the two should have been possible if the additional diffraction patterns with Pd attenuator had been recorded allowing a precise value of  $\lambda_{\min}$  to be identified.

Using the reflection intensity measurements, even though there were some shortcomings in the software development, and even though absorption effects have not been taken into account, showed that the diffraction patterns match PbCO<sub>3</sub> much better than SrCO<sub>3</sub>. Cerussite, PbCO<sub>3</sub>, is recognized to be a common impurity in rosasite (Cressey, 1994).

It was fortunate for us that the search procedure in the database *CDIF* allowed relative and absolute errors of the unit-cell dimensions to be specified separately. Absolute errors as great as 20% would probably not occur in other types of work, but when combined with a relative error of 0.5% or less, the number of matching compounds can be reduced to one or a very small number.

For crystallite B, the structure was determined with no prior assumptions except the chemical formula, and it appears to be identical to malachite, Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>. The absolute values of the unit-cell dimensions were only approximately established and are fortuitously close to the 'correct' ones shown in Table 1. The atom coordinates, which depend of course on the intensity measurements, are much less precisely determined than those from the

neutron diffraction study of Zigan, Joswig, Schuster & Mason (1977), but are in excellent agreement with them; the average differences are about one e.s.d., and the largest differences just over three e.s.d.'s.

The structure of rosasite remains unknown! Since we selected the largest available crystallites we conclude that while the bulk of the sample may be rosasite, the largest particles present are impurities.

In summary, Laue diffraction patterns have been recorded for crystallites with all dimensions <20 μm. In one case these diffraction patterns allowed identification of the crystallite, and in the other, despite very poor crystal quality, a complete structure determination was achieved.

We are grateful to EPSRC for financial support and the provision of synchrotron radiation facilities and its Chemical Database Service, and to many staff at Daresbury Laboratory for advice and assistance, and to Dr G. Cressey, Natural History Museum, London, for a sample, and for information on cerussite.

#### References

- Campbell, J. W. (1993). *Daresbury Laue Software Suite*. DRAL Daresbury Laboratory, Warrington WA4 4AD, UK.
- Campbell, J. W., Harding, M. M. & Kariuki, B. M. (1995). *J. Appl. Cryst.* **28**, 43–48.
- Carr, P. D., Cruickshank, D. W. J. & Harding, M. M. (1992). *J. Appl. Cryst.* **25**, 295–308.
- Carr, P. D., Dodd, I. M. & Harding, M. M. (1993) *J. Appl. Cryst.* **26**, 384–387.
- Chevrier, G., Giester, G., Heger, G., Jarosch, D., Woldner, M. & Zemmann, J. (1992). *Z. Kristallogr.* **199**, 67–74.
- Cressey, G. (1994). Personal communication.
- Dodd, I. M., Hao, Q., Harding, M. M. & Prince, S. M. (1994). *Acta Cryst.* **B50**, 441–447.
- Hao, Q., Harding, M. M. & Campbell, J. W. (1995). *J. Appl. Cryst.* **28**. In the press.
- Helliwell, J. R., Habash, J., Cruickshank, D. W. J., Harding, M. M., Greenhough, T. J., Campbell, J. W., Clifton, I. J., Elder, M., Machin, P. A., Papiz, M. Z. & Zurek, S. (1989). *J. Appl. Cryst.* **22**, 483–497.
- Jarosch, D. & Heger, G. (1988). *Bull. Min.* **139**, 111–142.
- Roberts, A., Jambor, J. & Grice, J. (1986). *Powder Diffr.* **1**, 56–57.
- Sheldrick, G. M. (1993). *SHELXL. Program for Structure Refinement*. Univ. of Göttingen, Germany.
- Zigan, F., Joswig, W., Schuster, H. D. & Mason, S. A. (1977). *Z. Kristallogr.* **145**, 412–426.

\* Lists of structure factors, anisotropic displacement parameters and details of the structure determination have been deposited with the IUCr (Reference: HE0117). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.