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A Test of the Importance of Weak Reflections in Resolving a Space-Group Ambiguity Involving the Presence or Absence of an Inversion Centre

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Abstract

The structure of margarite, $CaAl_2[Al_2Si_2O_{10}](OH)_2$, has been reported in space group $C2/c$, and in the corresponding non-centrosymmetric space group Cc. Previous refinements of margarite in space group Cc were marred by strong correlations affecting parameters that are inversion related in $C2/c$. Refinement of single-crystal X-ray diffraction data, collected with synchrotron radiation, converged without large correlations in Cc. The refinement was based on 4056 F_{obs}, without merging Friedel pairs, including all the weak reflections ($R = 0.027$). No atom in Cc is removed further than 0.08 Å from its corresponding position in $C2/c$. The R in space group $C2/c$, after merging of the Friedel mates, was 0.059 (2658 F_{obs}). For the weak F_{obs} the disagreement in space group $C2/c$ is much worse than in Cc. This agrees with the warning that it is the weak F_{obs} which are most sensitive to small non-centrosymmetric distortions [Schomaker & Marsh (1979). *Acta Cryst.* B35, 1933–1934]. Removing weak F_{obs} from the data results in a data set resembling one that could have been collected using an X-ray tube (with omission of weak F_{obs}). In the Cc model without weak F_{obs} many of the correlation coefficients rose dramatically to values

over 0.9, and consequently difficulties occurred in converging the refinement and the estimated standard deviations increased fourfold compared to the values obtained for refinement of the full data set. Therefore, if one wishes to resolve a space-group ambiguity: (1) one should collect precise data, and especially collect as many weak reflections as precisely as possible; (2) one should include all reflections in the refinement, even if this raises the R value – a more complete data set, with a higher R value may be more important in establishing the symmetry than a smaller data set with a lower R value; (3) when measuring at a synchrotron one should use a wavelength which emphasizes the anomalous-dispersion contribution in order to make the differences between the Friedel pairs more significant.

Introduction

Space group Cc has the distinction of being erroneously assigned most often in crystal structure determinations. At least 11% of all crystal structures determined in this space group actually have a higher symmetry (Baur & Kassner, 1992). Of 35 cases reported in which the symmetry of a crystal structure described originally in space group Cc was revised

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† Deceased 13 June 1990.

upwards, seven involved a space group in a more highly symmetric crystal system while 28 involved an overlooked inversion centre, that is the actual space group was found to be $C2/c$. Marsh (1986) has pointed out that a 'particularly bothersome situation arises when the choice is between a disordered structure in the centrosymmetric space group and an ordered (or a more ordered) structure in the non-centrosymmetric space group'. Baur & Tillmanns (1986) gave a number of recommendations about recognizing indications for having overlooked an inversion centre in the course of a crystal structure determination. However, it would be preferable to set up each diffraction experiment from the beginning in such a way that a possible ambiguity in the assignment of the space group is minimized in the first place. In this context the remarks of Schomaker & Marsh (1979) are useful: '...we emphasize that the reflections most crucial to the decision as to whether or not a crystal structure is centrosymmetric are the very weak ones, for it is these reflections that are most sensitive to the small imaginary components arising from non-centrosymmetric distortions. The common practice of deleting weak reflections from the data set may make it impossible to reach the correct decision.'

We decided to put the suggestion of Schomaker & Marsh (1979) to an experimental test by trying to discriminate between a centrosymmetric and a non-centrosymmetric model of a crystal which is nearly centrosymmetric, but not quite so. For this we used natural margarite, a Ca-containing mica, where the question arises as to whether it can be shown by X-ray diffraction that the tetrahedrally coordinated Al and Si atoms are ordered (space group Cc) or not (space group $C2/c$). Originally the crystal structure of margarite, $CaAl_2[Al_2Si_2O_{10}](OH)_2$, was determined by X-ray diffraction in the centrosymmetric space group $C2/c$ (Takeuchi, 1965) with Al and Si atoms occupying statistically two sets of equivalent positions. Later it was refined in the corresponding non-centrosymmetric space group Cc (Guggenheim & Bailey, 1975, 1978), with Al and Si atoms distributed in an ordered way over four equivalent positions. However, the refinements were marred by strong correlations (correlation coefficients up to 0.93 were encountered) affecting the parameters which would have been related by an inversion centre in the centrosymmetric space group $C2/c$. Consequently convergence was extremely slow in these refinements, the estimated standard deviations (e.s.d.'s) were high and it was reported to be impossible to refine aniso-tropic displacement parameters. A previous refinement of neutron diffraction data collected on margarite supported the lower symmetry, space group Cc (Joswig, Takeuchi & Fuess, 1983). All of the previously collected X-ray diffraction data sets were incomplete for a non-centrosymmetric structure with a significant dispersion contribution of an atom (Ca), since only one member of each Friedel pair was collected. The differences between the $F_{obs}(hkl)$ and the $F_{obs}(\bar{h}\bar{k}\bar{l})$ in the presence of anomalous scatterers are diagnostic of the absence of inversion centres in a crystal and can be identified without a structure-factor calculation just on the basis of the available F_{obs}. For non-centrosymmetric crystals the asymmetric region of the data set must include both members of each Friedel pair (Ibers, 1967). Without their presence a correct comparison of the symmetry options is at least less significant, or may even be meaningless.

The best way to obtain a very precise data set containing practically all of the accidentally absent F_{obs} as well as the very weak reflections is to collect the diffraction data from a fair-sized crystal using monochromatic synchrotron X-radiation. As a result of the high natural collimation of synchrotron radiation (divergence < 1 mrad in the X-ray region) and the small spectral width of the incoming beam ($\Delta\lambda/\lambda \simeq 4 \times 10^{-4}$ at $\lambda = 1$ Å) the width of the reflections is mainly determined by the mosaic spread of the sample crystal. As a result extremely narrow profiles down to 0.02° full width at half maximum (FWHM) may be encountered provided a good quality mosaic crystal is used (in the case of our sample values from 0.04 to 0.1° were observed). Together with the high intensity, this yields dramatically increased peak-to-background ratios and can make nearly all reflections observable, including those which in routine structure determinations, even if measured, are usually omitted because they fall below a certain limit, such as 1, 2 or 3 e.s.d.(F_{obs}).

We could have put Schomaker & Marsh's (1979) suggestion to the test without using any experimental data, by analyzing accordingly a suitably calculated 'synthetic' set of F_{calc}. However, we thought it more interesting, and more applicable to actual practice, to use a set of F_{obs}. To the best of our knowledge such a test has not been performed yet on a set of either measured or calculated structure-factor data. This is the more surprising as it is commonly agreed that weak reflections *should be important* for diagnosing the presence or absence of inversion centres (see *e.g.* Schwarzenbach *et al.*, 1989), but nevertheless they are usually omitted from refinements.

Experimental

The specimen of margarite comes from Greiner, Zillertal, Tirol, and is part of the same hand specimen as the sample used by Joswig *et al.* (1983) for a neutron diffraction study of this mineral. The chemical composition of margarite as determined by wet chemical analysis by these authors was assumed to

apply to our sample as well (Table 1). A crystal of margarite, ideal chemical formula $CaAl_2[Al_2Si_2O_{10}]$-$(OH)_2$, of approximate dimensions $380 \times 250 \times 70$ μm, yielded at three different occasions (several months apart) three data sets at the five-circle diffractometer at HASYLAB (Kupčik, Wulf, Wendschuh-Josties, Wolf & Pähler, 1986). In order to minimize the influence of absorption effects the wavelengths used were $\lambda = 0.6000$, 0.5607 and = 0.5614 Å. Data were collected essentially within a sphere of $\sin\theta/\lambda < 0.89$ Å^{-1}. Outside of this $\sin\theta/\lambda$ limit about 200 additional reflections, estimated to be strong, were measured individually. The cell constants were determined on a CAD-4 diffractometer with Mo $K\alpha$ radiation using 25 reflections between 17 and 24° in θ.

Initially each of the data sets was refined separately. Upon refinement of the structure the second data set gave unexpectedly large R values. To find the source of this, the ratios F_{obs}/F_{calc} were plotted against all available parameters such as reflection number, monitor count, polarization factor and setting angles of the diffractometer. At certain φ angles the observed intensities were found to be too small. The profiles of reflections within these φ intervals showed that they had been partially cut because we had selected the $2\theta/\theta$-scan mode for this data set by mistake. Apparently there was an error in the mechanical part of the φ circle (since corrected) which had been compensated in the prescan by an adjustment of the ω angle. But as ω was coupled to 2θ, this angle was misplaced. For most of the reflections the secondary beam stayed within the aperture of the detector, but for some it did not.

We found a way to identify reflections affected by this error without using the observed F_{obs}/F_{calc} deviation by comparing the expected and the actual peak positions: to minimize the differences and to maximize the reliability of the calculated positions the calculations had to include all possible sources of geometrical error (Kassner, 1988). By using the ω position at the maximum of every reflection the orientation matrix was refined together with the parameters of the geometrical errors thus minimizing the differences between measured and fitted diffraction vectors (Kassner, 1989a). The three-dimensional residuals were projected onto the one direction that was associated with the movement of the circle which interested us most, the φ circle. These exhibited a deviation with a period of about 13°, the tooth size of a worn-out gear. The geometrical refinement was also applied to the uncorrupted data sets, where the same deviations were present, but were of no consequence because the data were collected with pure ω scans and, therefore, suffered no cutting off of the profiles by 2θ misplacement of the detector aperture. Projecting the geometric residuals onto the direction

Table 1. *Crystal data, data collection and R values for margarite*

Chemical formula	$(Ca_{0.73}Na_{0.21})(Al_{2.01}Fe_{0.03}Mg_{0.10}$-$Li_{0.12})Si_{1.94}Al_{2.06}O_{10}(OH)_2$
Space group	Cc
a (Å)	5.1138 (2)
b (Å)	8.8569 (4)
c (Å)	19.1851 (10)
β (°)	95.484 (4)
V (Å^3)	864.96 (12)
Z	4
M_r	397.34
D_x (Mg m^{-3})	3.051
λ (synchrotron) (Å)	0.600, 0.5607, 0.5614
Scan	ω, $2\theta/\theta$, ω
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.89
μ(Ag $K\alpha$) (mm^{-1})	0.768
Transmission factors	0.782 to 0.949
λ(Mo $K\alpha$) (Å)	0.71069
Size of crystal (μm)	$380 \times 250 \times 70$
No. of I_{hkl} measured	7549
No. of I_{hkl} rejected (see text)	586
No. of nonunique I_{hkl}	6963
No. of unique I_{hkl} in Cc (N_{REF})	4056
No. of variables (N_{VAR})	177
$R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$	0.027
$wR = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{1/2}$	0.041
GoF = $[\Sigma w(F_o - F_c)^2/$ $(N_{REF} - N_{VAR})]^{1/2}$	4.0

associated with the 2θ circle, we identified 586 out of a total of 7549 non-unique reflections that were misplaced by more than $\pm 0.13°$ in 2θ. They were dropped from the structure-factor refinement and a total of 6963 F_{obs} was accepted.

The final data set was arrived at by correcting the I_{hkl} against two primary-beam monitors which measured the components parallel and normal to the electron-beam orbit of the synchrotron ring in order to get a polarization correction (Eichhorn, 1987a). The long-term drift, mainly as a result of the polarization dependence of the ratio of $I(000)$ over the monitor count, was corrected by evaluating the standard reflections (Kassner, 1989b) and the factors of the attenuating filters were refined as scale factors. Absorption was corrected by the analytical method (Davenport, Spadaccini & Stewart, 1990). Without averaging the Friedel pairs 4056 unique F_{obs} were obtained in this way. With the exception of I_{obs} $(1,\overline{15},\overline{1}) < 0.0$ and some reflections rejected for geometrical reasons (see above), each measured reflection was actually observed. In the data set of 4056 F_{obs} a total of four reflections have F_{obs} smaller than 3 e.s.d., and more than 50% of the F_{obs} are stronger than 87 e.s.d. All reflections, even those falling under the 3 e.s.d. limit, were used in the refinement. The e.s.d.'s of the measured intensities were based solely on the counting statistics. The weights were chosen proportional to $1/$e.s.d.^{2}.

Refinements

All refinements were performed with *CRYLSQ* (Olthof-Hazekamp, 1990) and are based on $|F|$

unless stated otherwise. Scattering factors and dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The scattering factors of $Al^{1.5+}$, Ca, H, Li, O^-, Si^{2+} were used, where the values for $Al^{1.5+}$ and Si^{2+} were obtained by interpolation. The values of f' and f'' of Ca for Ag $K\alpha$ radiation are 0.137 and 0.193, respectively; these and the corresponding, but smaller, values for Al, O and Si were used. The under-occupation of the Ca site and its Na content were modelled by refining the population factor of this site. Likewise the population factor of the Li site was varied (however, it is partly occupied by Mg). The H-atom positions and their population parameters were held constant at the values reported by Joswig *et al.* (1983). The isotropic displacement parameters of H and Li were kept constant at a value of $U = 0.02$ Å^2.

A full-matrix least-squares refinement of 4056 F_{obs} in space group Cc yielded an R value of 0.027 and a wR of 0.041 (Table 2). None of the correlation coefficients exceeded 0.9, in fact only three of them were larger than 0.8. Upon reversing polar axes (by changing the signs of the f'' contributions to the scattering factor) R rose to 0.029, and the mean e.s.d. of the coordinates of the O atoms increased from 0.0007 to 0.0008 Å. The structure factors most affected by reversing the polarity were those with magnitudes less than 5% of the strongest structure factors (compare Figs. 1a and 1b). A refinement in space group $C2/c$, after merging of the Friedel mates, resulted in an R of 0.059 for 2658 F_{obs}. For the weak F_{obs} the disagreement in space group $C2/c$ (Fig. 1c) is much worse than in Cc.

After removing from our data set all F_{obs} observed to be smaller than about 5% of the strongest reflections ($F_{obs} > 15.0$) the R values were 0.027 for 2676

Table 2. *Various refinements for margarite*

The table includes the number of observations used in refinement ($\#F_o$); the number of refined parameters ($\#P$); the R and wR values (for definitions see Table 1), goodness of fit (GoF); mean e.s.d. of coordinates of O atoms [σ(O) in Å], number of correlation coefficients exceeding 0.9 ($\#cc$) and references (Ref.). All refinements were performed by full-matrix least squares with anisotropic displacement parameters (DP's) unless otherwise stated; X-ray data except for neutron data (N), lines 12 and 13; xe is the enantiomorph-polarity parameter (Flack, 1983).

Space group	$\#F_o$	$\#P$	R	wR	GoF	e.s.d.(O)	$\#cc$	Ref.	Remarks
Cc	4056	177	0.027	0.041	4.0	0.0007	0	(a)	All F_{obs}
Cc	4056	177	0.029	0.046	4.5	0.0008	0	(a)	Alternate orientation
Cc	2676	177	0.027	0.031	3.1	0.0028	11	(a)	$F_{obs} > 15$
Cc	2711	177	0.027	0.042	4.3	0.0008	0	(a)	W/o filter
Cc	4056	178	0.027	0.039	3.6	0.0010	1	(u)	All F_{obs}; xe = 0.006 (29)
Cc	2676	178	0.027	0.032	3.0	0.0039	25	(a)	$F_{obs} > 15$; xe = 0.209 (126)
Cc	2711	178	0.028	0.040	3.8	0.0011	1	(a)	W/o filter; xe = 0.007 (31)
Cc	4056	83	0.040	0.061	5.5	0.0013	0	(a)	All F_{obs}; xe = −0.007 (44) Isotropic DP
$C2/c$	2658	91	0.059	0.151	15.3	0.0016	0	(a)	All F_{obs}
$C2/c$	1712	91	0.038	0.077	8.8	0.0019	0	(a)	$F_{obs} > 15$
$C2/c$	1925	91	0.098	0.175	18.1	0.0019	0	(a)	W/o filter
Cc	1037	217	0.020	0.013	1.9	0.0036	0	(a)	N, ref. (b) rerefined
Cc	1003	217	0.017	—	—	0.0014	0	(b)	N, blocked
Cc	1071	75	0.040	0.052	1.4	0.0065	12	(c)	Isotropic DP
$C2/c$	1071	87	0.049	0.077	2.1	0.0032	0	(c)	--
Cc	1071	76	0.075	0.095	—	0.0086	0	(d)	Blocked
$C2/c$	1071	40	0.084	0.107	—	—	0	(d)	Isotropic DP

References: (a) this work; (b) Joswig *et al.* (1983); (c), (d) Guggenheim & Bailey (1978, 1975).

F_{obs} [mean e.s.d.(O) = 0.0031 Å] in space group Cc, and 0.038 for 1712 F_{obs} [e.s.d.(O) = 0.0019 Å] in $C2/c$. By omitting the weak reflections the refinement of the model in space group Cc yielded 11 correlation coefficients exceeding 0.9. These involved parameters of atoms pseudosymmetrically related in Cc (which would be equivalent in space group $C2/c$). Consequently convergence was slow and the e.s.d.'s were larger by a factor of four compared to the values in the refinement with the full data set.
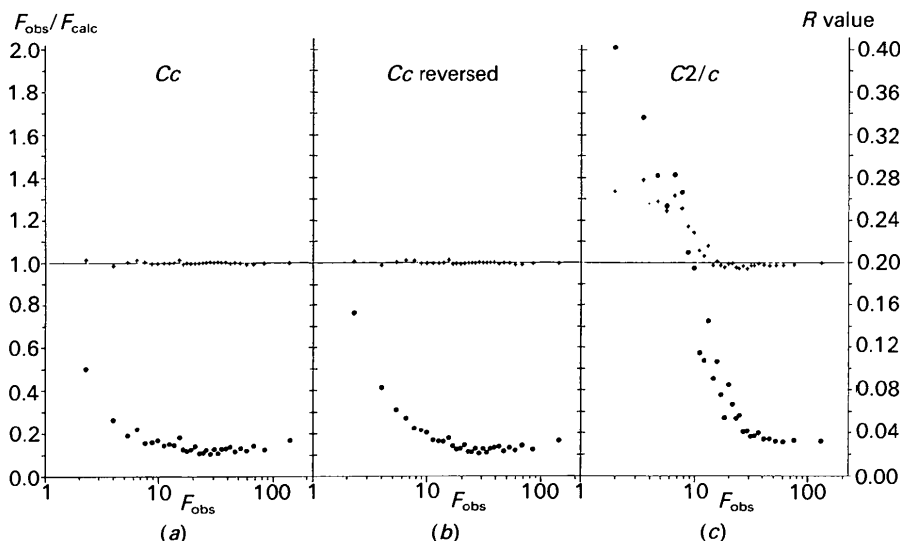

Fig. 1. (a) Ratio of $\Sigma F_{obs}/\Sigma F_{calc}$ (crosses) and R values (circles), each in groups of 135 reflections, plotted against group averages of F_{obs} in logarithmic scale for the refinement of margarite with 4056 F_{obs} in space group Cc ($R = 0.027$). (b) Same as (a) also in space group Cc, but assuming an inverse orientation of the crystal ($R = 0.029$). (c) Same type of values as in (a), but in groups of 88 reflections for the refinement of margarite with 2658 F_{obs} in space group $C2/c$ ($R = 0.059$).

A data set with a preponderance of weak reflections was generated by using only those measurements for which an attenuator filter was not needed during data collection. This gave us the opposite, namely a refinement of a similar number of weak reflections as before, the strongest of which were about 20% in magnitude as compared to the strongest F_{obs}. This resulted in an R value of 0.027 for 2711 F_{obs} [mean e.s.d.(O) = 0.0008 Å] in Cc, and no correlation or convergence problems were apparent. The corresponding R in space group C/c was 0.098 for 1925 F_{obs} [mean e.s.d.(O) = 0.0019 Å]; thus the discrimination between the model with and without an inversion centre was sharpened.

For completeness we also tested for the presence of inversion twinning in our sample using Flack's (1983) algorithm (see lines 5 to 7 in Table 2). Each of the refinements commenced at an xe (Flack calls it x, but we wish to avoid any confusion with an x coordinate, in $CRYLSQ$ it is called xabs) value of 0.5, i.e. it was assumed that our sample was composed of two individuals inverted to each other (of opposite polarity) and of equal volume. The refinements of all the data (line 5), and of the data set with a preponderance of weak reflections (line 7) gave values of xe close to and statistically identical to zero. The data without the weak reflections (line 6) yielded an xe value of 0.21. This is within 1.6 e.s.d. of zero but also only within 2.3 e.s.d. of 0.5. This shows once again that this reduced data set has only a diminished (or no) significance for deciding the question of the presence or absence of an inversion centre and/or inversion twinning. Interestingly, the convergence of this refinement was even worse (25 correlation coefficients exceeding 0.9) than for the refinement without the parameter xe (line 3). Moreover the displacement parameters of atom O(62) became not positive-definite.

Marsh (1981) suggested, because 'two isotropic atoms in a slightly non-centrosymmetric array can closely approximate, in $|F|$ values, a pair of anisotropic atoms in a centrosymmetric array', to compare in such cases a refinement of the centrosymmetric structure with anisotropic displacement parameters with a refinement of the non-centrosymmetric structure with isotropic displacement factors for the atoms. Therefore, we compare refinements with similar numbers of variable parameters, thus making the comparison fairer. In our case such a refinement again clearly favours space group Cc for margarite (compare lines 8 and 9 of Table 2). A referee suggested that for this type of study the refinement should have been based on $|F|^2$ instead of on $|F|$.

This is not necessarily so: 'apart from a possible bias when refining on $|F|$, the main difference between refinements on $|F|$ and $|F|^2$ is equivalent to an up-weighting of weak reflections if $\sigma(|F|)$ is kept finite for $|F| = 0$' (Schwarzenbach et al., 1989). As only a few reflections are (nearly) unobserved, neither the down-weighting [to $w(|F|) = 0$] of reflections below $|F| = 0$ (or any other limit) nor the up-weighting of reflections directly above that limit occurs in our case in a statistically significant way. Nevertheless, we made refinements based on $|F|$ and $|F|^2$ and found that it made little difference how they were performed. As expected in the $|F|^2$ case the R values were about twice as high as those reported for the refinements listed in Table 2, the goodness of fit and the e.s.d.'s were comparable, the refined values of the parameters themselves were similar (on average within two standard deviations), and the high correlation coefficients showed up in the same places. Generally, of course, a refinement based on $|F|^2$ is preferable (in order to avoid the changes in weighting), even though we are not aware that anybody has yet shown that a refinement based on $|F|$ resulted in an incorrect crystal structure determination because it was based on $|F|$. The omission of weak reflections, on the other hand, has clearly contributed to incorrect choices in cases of centrosymmetric/non-centrosymmetric ambiguities.

Table 3 shows the positional coordinates and the U_{eq} of margarite.* The main bond lengths are given in Table 4. Polyhedral $STRUPLO$ diagrams of margarite are presented as Figs. 2 and 3. All these are based on the refinement of the full data set of 4056 F_{obs} in space group Cc. Computer programs used in the course of this work include: $DIF4$ (Langhoff, 1983) in a modified version (Wendschuh-Josties & Wulf, 1989), $REDUCE$ and $AVSORT$ (Eichhorn, 1987a,b), $GEOERROR$ and $DRIFT$ (Kassner, 1989a,b), $NORM80$ (Main et al., 1980), $ABSORB$ (Davenport et al., 1990), $CRYLSQ$ (Olthof-Hazekamp, 1990), $SADIAN90$ (Baur & Kassner, 1991), and $STRUPLO90$ (Fischer, le Lirzin, Kassner & Rüdinger, 1991).

Results and discussion

The role of weak reflections

Our results show that it is possible to resolve a space-group ambiguity between a non-centrosymmetric space group and the corresponding centrosymmetric space group as long as the weak reflections are measured with sufficient precision and are used in the least-squares refinement. It is the

Table 3. Coordinates, U_{eq} (Å²) and population factors (Pop) for margarite

	x	y	z	U_{eq}	Pop
Ca	0.5000	0.59368 (2)	0.25000	0.00994	0.922 (2)
Al(2)	0.24793 (12)	0.41685 (3)	-0.00005 (3)	0.00472	1.0
Al(3)	0.75176 (12)	0.58487 (3)	0.00007 (3)	0.00481	1.0
Al(11)	0.96396 (10)	0.42742 (4)	0.14210 (2)	0.00446	1.0
Al(22)	0.04730 (10)	0.24379 (4)	-0.14210 (3)	0.00468	1.0
Si(12)	0.03520 (10)	0.57426 (3)	-0.14475 (2)	0.00422	1.0
Si(21)	0.45452 (9)	0.25689 (3)	0.14471 (2)	0.00410	1.0
O(11)	0.96100 (17)	0.44541 (9)	0.05243 (4)	0.00610	1.0
O(12)	0.04423 (18)	0.56128 (9)	-0.05974 (4)	0.00631	1.0
O(21)	0.39490 (17)	0.25395 (7)	0.05975 (5)	0.00613	1.0
O(22)	0.11932 (17)	0.24913 (8)	-0.05220 (4)	0.00567	1.0
O(31)	0.86384 (19)	0.59802 (7)	0.17752 (5)	0.00693	1.0
O(32)	0.13699 (21)	0.58209 (8)	0.32283 (5)	0.00724	1.0
O(41)	0.26702 (16)	0.77908 (8)	0.16783 (4)	0.00710	1.0
O(42)	0.71246 (16)	0.78451 (8)	0.33196 (5)	0.00743	1.0
O(51)	0.28810 (17)	0.39066 (9)	0.17846 (5)	0.00727	1.0
O(52)	0.73464 (18)	0.39630 (9)	0.32126 (5)	0.00694	1.0
O(61)	0.45296 (19)	0.56631 (10)	0.05133 (5)	0.00742	1.0
O(62)	0.54755 (18)	0.43577 (9)	-0.05129 (5)	0.00791	1.0
H(11)	0.3663	0.65500	0.06200	0.02	0.77
H(12)	0.6325	0.34520	-0.06040	0.02	0.79
H(21)	0.4390	0.59100	0.09800	0.02	0.21
H(22)	0.5610	0.60100	0.40500	0.02	0.21
Li	0.2514 (20)	0.7545 (8)	-0.0011 (6)	0.02	0.452 (12)

Table 4. Bond lengths (Å) for margarite

Al(11)—O(11)	1.7263 (9)		Al(22)—O(22)	1.7295 (10)
Al(11)—O(31)	1.7531 (8)		Al(22)—O(42)	1.7549 (9)
Al(11)—O(41)	1.7547 (8)		Al(22)—O(52)	1.7550 (9)
Al(11)—O(51)	1.7661 (9)		Al(22)—O(32)	1.7608 (9)
Mean	1.7501		Mean	1.7501
Si(12)—O(32)	1.6240 (8)		Si(21)—O(31)	1.6270 (8)
Si(12)—O(12)	1.6312 (9)		Si(21)—O(51)	1.6287 (9)
Si(12)—O(42)	1.6320 (8)		Si(21)—O(41)	1.6290 (9)
Si(12)—O(52)	1.6322 (10)		Si(21)—O(21)	1.6295 (10)
Mean	1.6299		Mean	1.6286
Al(2)—O(11)	1.8743 (10)		Al(3)—O(22)	1.8577 (8)
Al(2)—O(22)	1.8747 (8)		Al(3)—O(11)	1.8639 (9)
Al(2)—O(61)	1.9041 (10)		Al(3)—O(62)	1.8996 (10)
Al(2)—O(62)	1.9053 (10)		Al(3)—O(61)	1.9016 (11)
Al(2)—O(21)	1.9488 (9)		Al(3)—O(12)	1.9812 (10)
Al(2)—O(12)	1.9506 (9)		Al(3)—O(21)	1.9822 (9)
Mean	1.9096		Mean	1.9144
Ca—O(31)	2.4272 (9)		Li—O(62)	2.098 (9)
Ca—O(32)	2.4300 (10)		Li—O(61)	2.157 (9)
Ca—O(51)	2.4509 (9)		Li—O(11)	2.203 (9)
Ca—O(52)	2.4599 (9)		Li—O(22)	2.204 (10)
Ca—O(42)	2.4866 (8)		Li—O(12)	2.256 (9)
Ca—O(41)	2.4984 (7)		Li—O(21)	2.257 (10)
Mean	2.4588		Mean	2.196

Fig. 2. Perspective polyhedral *STRUPLO* plot of margarite viewed parallel to the layer in direction [100]. The coordination octahedra (Al at the centre) are densely hatched, the coordination tetrahedra around Al are lightly hatched, the Si tetrahedra remain white. The third octahedral cation (Li) is shown as a small circle within the plane of the Al octahedra. The interlayer cations (Ca) are shown as large circles. The octahedral layer sandwiched between two tetrahedral sheets stands out clearly. The outline of the unit cell is indicated.

Fig. 3. Perspective *STRUPLO* plot of one layer of margarite looking in a direction 20° off [001]. For explanations see Fig. 2. The octahedral part of the layer and the lower tetrahedral sheet are shown throughout. The upper tetrahedral sheet displays the alternation of Si and Al tetrahedra. This is only shown on the left side, thus providing a better view of other parts of the crystal structure.

presence of the weak F_{obs} in our data set which makes it possible to refine the crystal structure of margarite in space group *Cc* without bothersome correlations affecting related parameters. Correlation coefficients greater than 0.9 significantly increase the estimated standard deviations of the related parameters. This may lead to not positive-definite displacement parameters (DP) or in extreme cases to a divergence of the least-squares refinement. In this way the least-squares algorithm informs us that we are trying to refine a nonsensical model, that is a model which is not supported by the quality or the number of the available observations.

The high precision of our measurement is not the main reason responsible for the observed absence of high correlations. This is demonstrated by the
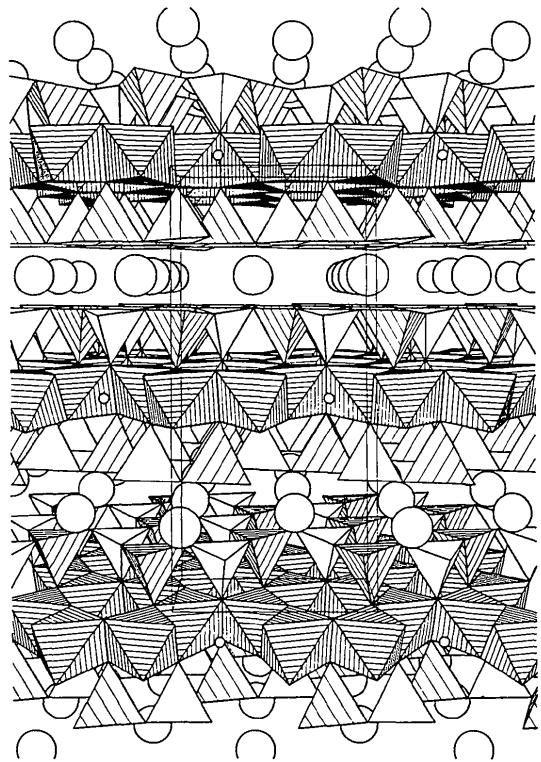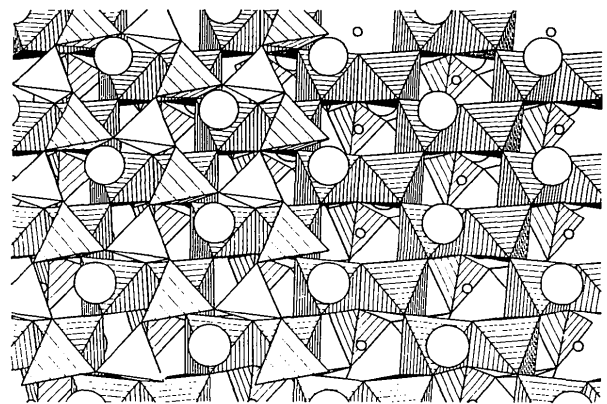
refinement of our data set in which the weak reflections were systematically omitted: in this case correlation coefficients over 0.9 appeared (Table 2, line 3). A plot of this refinement analogous to Fig. 1(a) looks just like Fig. 1(a) but with the first ten points on the left omitted. It is not a question of the smaller number of F_{obs} in the data set, either. When we use approximately the same number of reflections in a refinement as in the data set without weak observations, but systematically leave out the strong reflections, a normal refinement without strong correlations is obtained (Table 2, line 4). The weak observations are not heavily concentrated at high $\sin\theta/\lambda$ values; thus the omission of the weak reflections and, consequently, the increased correlations are not caused by a selective omission of high-order reflections. A plot analogous to Fig. 1(a), but displaying the groups of R values as a function of $\sin\theta/\lambda$ shows that the R values do not increase with $\sin\theta/\lambda$ at all. In this context it is important that the ratio (mean F_{obs})/(mean F_{calc}) remains close to unity even for the weak F_{obs} (Fig. 1a).

The weak reflections are also most sensitive to the two possible orientations of the crystal relative to the incoming X-ray beam (Fig. 1a as compared with Fig. 1b, see also lines 1 and 2 in Table 2). There is a measurable difference between Friedel mates even in a case where the strongest anomalous scatterer (Ca) is far removed from the absorption edge. This demonstrates that it is useful to investigate closely the differences between Friedel pairs when trying to resolve a space-group ambiguity. Of course this has been known for a long time (Ibers, 1967) but is rarely applied. Interestingly, the ratio between the f''/f of Ca for Ag $K\alpha$ radiation (around 0.01 at small values of $\sin\theta/\lambda$) is similar to the ratios of f''/f of oxygen for Cr $K\alpha$ and Fe $K\alpha$ radiation. This means that when establishing the absolute configuration in organic compounds oxygen can be regarded as an anomalous scatterer at wavelengths of about 2 Å.

The data set in which we had omitted the weak reflections ($F_{obs} < 15.0$) is an approximation to a standard data set which could have been collected at an X-ray tube and where all F_{obs} smaller than about 2 e.s.d.(F_{obs}) had been omitted. Thus it resembles the data used by Guggenheim & Bailey (1975, 1978). It is very likely that with a conventional tube X-ray source one could get data which would fall somewhere in between the data we obtained and those usually measured. In order to achieve this one would have to spend a longer time in measuring weak reflections and one should refrain from employing any cutting off of observations in terms of e.s.d.(F_{obs}). It is apparent from Table 2 that the more the strong reflections are favoured (that is the weak reflections omitted), the closer the values of R become to each other for the Cc and the $C2/c$

models. That means we are losing the chance to resolve the space-group ambiguity if we do not have sufficiently large numbers of weak reflections. The much lower wR value (0.031, see line 3 of Table 2) for the refinement without the weak reflections as compared with the wR (0.041, see line 4) for the full data set, does not compensate for the loss of definition of the crystal structure as shown by the strong correlations and the high estimated standard deviations.

In this context it is very instructive to compare the ratios $\Sigma F_{obs}/\Sigma F_{calc}$ (sorted in groups according to the magnitude of F_{obs}) for the weak reflections for the non-centrosymmetric model (Fig. 1a) with the centrosymmetric model (Fig. 1c). It is obvious that the calculated structure factors in space group $C2/c$ do not model the statistics of the intensity distribution of the weak observations, thus even in an almost centrosymmetric crystal structure the statistics of the intensity distribution are clearly non-centrosymmetric on the part of the weak reflections. This is indicated for the small values of z (< 0.12) in the overall $N(z)$ statistic of margarite prepared according to Howells, Phillips & Rogers (1950) as shown in Fig. 4 [E values calculated by the computer program $NORM$80, Main et al. (1980)]. The deviation from the centrosymmetric distribution is so slight that it could easily be overlooked. If Fig. 4 were plotted with the usual interval in z, and the weak reflections measured here were not included, the deviation from centrosymmetric would not be apparent at all. In contrast, the ratio $\Sigma F_{obs}/\Sigma F_{calc}$ deviates up to 40% from unity for the groups of weak reflections, while it stays close to one for the stronger reflections. This is the reason why the refinements of margarite by Guggenheim & Bailey (1975, 1978), where weak reflections must have been absent, remained essentially inconclusive as far as resolving the space-group ambiguity is concerned. Blocking of inversion-centre-related parameters into separate matrices during refinement (Guggenheim & Bailey, 1975) does not solve the problem as long as the diffraction data which can discriminate between different models are missing. One runs the danger of obtaining systematically incorrect results. However, the same danger is present if in full-matrix refinement extreme correlations are encountered. The only solution is to measure diffraction data which are sensitive in discriminating between the models in question, i.e. one must measure the weak reflections as already suggested by Schomaker & Marsh (1979). In practice this means that one must use longer counting times for measuring the weaker reflections.

In the particular case of margarite the refinement of neutron diffraction data proved helpful (Joswig et al., 1983) because the scattering lengths of Si and Al are more distinct from each other than their X-ray

scattering factors. In this case our full-matrix rerefinement of the neutron diffraction data, which orginally had been refined in blocks, confirmed the ordering of Si and Al atoms over separate sites in space group *Cc*. None of the correlation coefficients exceeded the crucial value of 0.9, but so many of them had correlation coefficients between 0.8 to 0.9 that the mean e.s.d.(O) level resulting from the full-matrix refinement is rather large, especially when one considers that the O atom is the heavy atom in this refinement (Table 2, lines 12 and 13).

No atom in *Cc* is removed further than 0.08 Å from its corresponding position in *C2/c*; the average distance is 0.05 Å. Such distances between pseudo-symmetric positions are shorter than those which an atom travels as a result of thermal vibrations. In view of the usual experience it may be surprising that diffraction methods can resolve atoms at such close distances from the images of their pseudosymmetric partners.

Structural results on margarite

The bond lengths determined here for the margarite from Greiner, Zillertal, Tirol, agree essentially with those found previously by neutron diffraction, but are more precise (Table 4). The mean Al—O distances in the two coordination tetrahedra (1.7501 Å) are identical to each other and agree very well with the mean value of 1.752 Å reported by Baur (1981) for 160 tetrahedral Al—O distances. This indicates that these are pure Al—O tetrahedra without any partial statistical occupancy by silicon. The mean Si—O distances in the coordination tetra-hedra around Si(12), 1.6299, and Si(21), 1.6286 Å,

are essentially identical within their statistical margin of error. The mean distance Si—O is estimated to be 1.622 Å for a pure silicate tetrahedron connected to three neighbouring coordination tetrahedra, taking into account the values of the angles Si—O—*T* (where *T* could be Al, B, Ga, P or Si) and the coordination numbers of the O atoms. This estimate is based on equation (7) from Baur (1978). According to the interpretation of the chemical analysis of the margarite from Greiner, Zillertal (Table 1), there is an excess of 3% Al in the tetrahedral portion of this margarite. This would amount to a lengthening of the mean Si—O distance by 0.004 Å [0.03 × (1.752 − 1.622)], and bring the expected tetrahedral (Si,Al)—O distance to 1.626 Å, only a little short of the observed value of 1.629 Å.

Since the mean tetrahedral Al—O and Si—O distances in the two crystallographically independent tetrahedral layers of margarite are identical there is no asymmetry in the distribution of tetrahedral Al in these layers as was claimed for margarite from Chester County, Pennsylvania (Guggenheim & Bailey, 1978). This could either mean that the two margarites are really different, or more likely, that the previous refinement was faulty as a result of the large correlations between positional coordinates (Table 2, line 14).

The individual Si—O distances range from 1.6240 (8) to 1.6322 (10) Å (Table 4), the individual tetrahedral Al—O distances from 1.7263 (9) to 1.7661 (9) Å, a much larger spread than for Si—O. In fact the average bond length of the two terminal Al—O distances is 1.7279 Å, while the mean of the six bridging Al—O bond lengths is 1.7574 Å for a difference of close to 0.03 Å. The Pauling bond strength received by the terminal O atoms O(11) and O(22) is 1.83 valence units (v.u.) and for the bridging O atoms it is 2.078 v.u. This assumes that the Li position is half occupied by Li in sixfold coordination. From this one can calculate, using the extended electrostatic valence rule [Baur, 1981, equations (11) and (12)], an estimated bond length of 1.733 Å for the terminal Al—O bond and of 1.755 Å for the bridging Al—O bonds. If the contribution from the Li site (the species occupying it are uncertain anyhow) is neglected the bond strength received by the terminal O atoms is 1.75 v.u. and the estimated bond lengths for the terminal Al—O and the bridging Al—O distances are 1.727 and 1.757 Å, in almost perfect agreement with the corresponding observed mean Al—O distances.
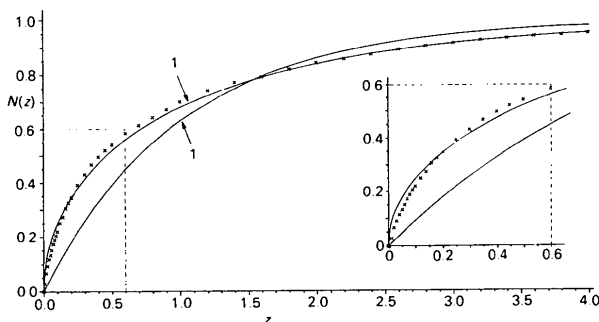

Fig. 4. Intensity-distribution curve (Howells *et al.*, 1950; Main *et al.*, 1980) for margarite for 4710 reflections within a sphere of $\sin\theta/\lambda = 0.89$ Å^{-1} obtained by a full expansion of all Friedel pairs (circles) compared with the expected values for centrosymmetric ($\bar{1}$) and non-centrosymmetric (1) crystal structures (curves). The fraction of reflections with values of *E* less than or equal to *z* is called *N*(*z*). The inset shows the low-*E* end of the distribution spread in the direction of *z*. The curve for margarite deviates from the theoretical centrosymmetric curve towards the theoretical non-centrosymmetric distribution only at values of *z* smaller than 0.12.

Concluding remarks

There never was any doubt about the general correctness and sound theoretical basis of Schomaker & Marsh's (1979) suggestion about the

importance of the weak reflections in resolving the centrosymmetric/non-centrosymmetric ambiguity. However, this work has shown that the contribution of the weak $|F|$ is really significant relative to the strong reflections in removing the strong correlations between pseudosymmetrically related pairs of parameters. From our experience the following can be learnt about strategies for determining crystal structures with small deviations from centrosymmetry.

(1) One should collect precise data, and especially collect as many weak reflections as precisely as possible. This means that one should spend longer counting times on weak rather than on strong reflections.

(2) All reflections should be included in the refinement, even if this raises the R value. A more complete data set, with a higher R value may do more for establishing the symmetry than a smaller data set with a lower R value. Weak reflections should never be discarded, because by neglecting them we are introducing an unnecessary systematic error into our measurement.

(3) The deviation from unity of the ratio $\sum F_{obs}/\sum F_{calc}$ (sorted in groups according to the magnitude of F_{obs}) for the weak reflections is a much more sensitive indicator of the correct model than the usual $N(z)$ statistic (compare Figs. 1a and 1c with Fig. 4). Therefore, such plots should be inspected before making a decision about the correct space-group assignment in each particular case. However, it can only be applied after the F_{calc} are available.

(4) Whether the refinements are based on $|F|$, or on $|F|^2$, care should be taken that the weak reflections are not unnecessarily down-weighted.

(5) When measuring at a synchrotron a wavelength should be used which emphasizes the anomalous-dispersion correction in order to make the differences between the Friedel pairs as large as possible. In doing so, however, one might encounter problems with stronger absorption.

(6) Anomalous dispersion should be used for the determination of the point group and therefore the space group as well. This means that both members of each Friedel pair should be measured.

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