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Compounds with the Marcasite Type Crystal Structure

VIII.* Redetermination of the Prototype

G. BROSTIGEN, A. KJEKSHUS and CHR. RØMMING

Kjemisk Institutt, Universitetet i Oslo, Blindern, Oslo 3, Norway

The crystal structure of marcasite (FeS_2-*m*) has been redetermined, and contrary to an earlier suggestion the mirror plane perpendicular to [001] at $z = \frac{1}{2}$ (and $z = 0$) appears to be present. The different result is chiefly attributed to an improved absorption correction in the present case.

One problem connected with the detailed studies on compounds with the pyrite (FeS_2-*p*), marcasite (FeS_2-*m*), and arsenopyrite (FeAsS; binary prototype $CoSb_2$) type structures, which recently have been carried out at this Institute, concerns the proper crystallographic symmetry of the FeS_2-*m* type structure. Diffraction data for the compounds with this structure type show systematic extinctions consistent with the space groups *Pnnm* and *Pnn*2. The choice of space group has previously [1,2] been considered for $FeSb_2$, FeS_2, $FeTe_2$, and $CoTe_2$, with the conclusion that the mirror plane characteristic of the higher symmetric space group *Pnnm* is absent. Of the two ways in which the mirror plane may be absent (*viz.* in terms of positional or thermal parameters), it was reported that the absence is of the first kind for $FeSb_2$,[1] of the second for $CoTe_2$,[2] and of both kinds for $FeTe_2$ [2] and possibly FeS_2.[2]

The experimental and computational means employed in these investigations have been improved on in several respects. Firstly, counter techniques have been substituted for the photographic measurement of the intensities of the scattered X-rays. Secondly, the recent availability of more suitable computer programmes allows corrections for dispersion to be made. Also, the specimen used could be given a shape convenient for absorption correction. The prototype FeS_2-*m* was singled out for a careful reexamination in which these and other possible improvements could be taken into account. This choice was in part indicated by the anomalous thermal vibrational parameters previously found for the sulphur atoms in FeS_2-*m*.[2]

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EXPERIMENTAL

The single crystals were chosen from a natural *marcasite* sample (Joplin, U.S.A.) kindly donated by Mineralogisk-Geologisk Museum, Universitetet i Oslo. The analytical data for this specimen are given in the preceding paper.[2]

Three dimensional intensity data were collected with an automatic Picker diffractometer using monochromatized Mo$K\alpha$-radiation. The $\omega - 2\theta$ scan technique was utilized at a scan speed of 1° min^{-1}. The background was measured at each of the scan range limits. The intensities of three selected test reflections, measured for every 50th reflection during the data collection, demonstrated a systematic variation which was corrected for in the sets of observed intensities. A 1 % addition for the uncertainty in the rescaling as well as for reducing the effect of systematic errors in the strong reflections, was included in the estimated standard deviation of the intensities from counting statistics.

The first set of intensity data was collected for a carefully selected, but crude single crystal fragment as isolated from the natural specimen. The shape and orientation of the crystal in relation to the diffractometer ϕ axis were obtained with the aid of an optical goniometer in combination with a travelling microscope. A graphite crystal was used for monochromatization, the scan range was $2\theta(\alpha_1) - 0.9$ to $2\theta(\alpha_2) + 0.9°$, and the background was measured for 60 s on each side of the reflections. 791 independent reflections with sin θ/λ up to 1.35 were explored for this crystal, of which only four proved to have a net intensity smaller than twice the estimated standard deviation.

The second crystal was ground into a nearly perfect sphere of 0.44 mm diameter. In this case a quartz single crystal monochromator was used, the scan range was increased by 0.2° (*vide supra*), and the background was measured for 15 s at each of the scan range limits. Out of the 760 independent reflections with sin $\theta/\lambda < 1.28$, 726 were larger than twice their estimated standard deviations; these were regarded as "observed" reflections and used in the subsequent calculations.

The intensities were corrected for the combined Lorentz and polarization factors, and for absorption and secondary extinction according to the actual shape of the crystal.

Calculations were performed on a CD 3300 computer using a set of programmes by Dahl *et al.*[3] Atomic scattering factors were taken from Hanson *et al.*[4] and the values for the real and imaginary parts of the dispersion from Cromer.[5] Anisotropic thermal motion of the atoms were allowed for according to the expression $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. The significance test of Hamilton[6] was used to assess the probable correctness of various computational models for the structure. (The observed and calculated structure factor data are available from the authors upon request.)

RESULTS AND DISCUSSION

Parallel with the presentation and discussion of the results it is convenient to comment on some more methodical and philosophical questions which arise in this connection.

The two marcasite crystals investigated here as well as that of the preceding study[2] were selected from adjacent spots on the same mineral specimen. Hence, it is probably reasonable to assume that these crystals are virtually identical with regard to chemical and physical perfection. The fact that one of the crystals had been subjected to light mechanical grinding does not apparently invalidate the assumption. On the other hand, this represents the first of a series of hypotheses or unevaluated approximations of the study.

One set of intensity data was collected for each of the crystals, *viz.* two sets of counter-diffractometer measurements and in addition the photographic recordings dealt with in Ref. 2. The question concerning whether one of the data sets *a priori* is more correct than the others immediately enforces a full discussion of systematic and random errors. These problems are considered in detail by, *e.g.*, Lonsdale *et al.*[7] and are not repeated here.

In relation to the absorption correction it is significant to dwell on the fact that two of the crystals had their natural shapes whereas the third had been ground to a nearly

perfect sphere. There is in the first place inevitable inaccuracies in the description of habits and the measurement of dimensions for the naturally shaped crystals. Secondly, limitations inherent in the available computer programme impose approximations in the mathematical definitions of the crystalline forms. The overall size of one of these crystals was, moreover, just amenable for treatment of the absorption correction by the computer programme. The absorption in the spherical crystal can, on the other hand, be corrected for completely, apart from more trivial errors caused by deviations from spherical symmetry, incorrect crystal diameter, and/or inaccurate linear absorption coefficients. Similar considerations apply to the correction for secondary extinction although the consequences of any inaccuracy are less important in the latter case.

Another source of uncertainty lies in the choice of atomic scattering factors. The complete electron distribution within the unit cell (*viz.* based on *ab initio* calculations or a hitherto unknown experimental technique) must be available in order to design entirely satisfactory scattering factors. However, even if the necessary information on the chemical bonding was at hand, the resulting "scattering factors" would become complicated and cumbrous multiparameter functions. Furthermore, the conventional crystallographic parameters are paradoxically explicitly contained in the more comprehensive conception of the complete electron distribution. The scattering factor problem can fortunately be considerably reduced by taking into account only those reflections with relatively large values for $\sin \theta/\lambda$ ($\geqq 0.6$ in the present case), where the contributions from the bonding electrons are small. The settling of the boundaries to the atomic cores is nevertheless a relevant source of ambiguity in the general case. However, the cores of sulphur and iron must, at any rate, contain a large proportion of the total number of electrons for the corresponding free atoms and according to calculations the actual selection of core boundaries appears to be rather unimportant. Thus, the customary scattering factors for neutral sulphur and iron could be employed, probably without any significant loss of accuracy.

The effects of dispersion may be taken into account by representing the atomic scattering factors of both kinds of atoms as complex variables of the diffraction angle. In the treatment of the photographic intensity data [2] it appeared to be a reasonable approximation to neglect these effects, whereas they ought not to be disregarded in connection with the improved accuracy of the two sets of counter data. In fact, a crucial part of the present problem centres around the dispersion effects (*vide infra*).

Anharmonic effects are clearly present in any real crystal, but in view of the time required to develop the theory for the general problem with anharmonicity in admixture with anisotropic thermal vibration and afterwards preparing a computer programme dealing with this considerably more complex case it was decided to utilize the facilities already at hand. The harmonic model appears to represent a useful approximation in the present case where the results show that the root mean square amplitudes in the direction of main axes of vibration are almost equal (0.063, 0.062, and 0.059 Å for Fe and 0.069, 0.069, and 0.064 Å for S are obtained for spherical crystal), implying that the thermal motions of both kinds of atoms are very nearly isotropic.

The weighting of the intensity data constitutes a side of the computational work which are open to some degree of freedom for subjective judgements. The weighting schemes in this work were based on counting statistics; careful analyses showed that this does not represent a relevant source of error.

The least squares refinement procedure was continued until no shifts were produced in any variable. Different sets of input parameters were tried in order to ascertain that none of the least squares refinements were terminated at secondary (false) minima.

Apart from making allowance for the effects of dispersion the computational models were essentially the same as those considered previously.[2] It should be emphasized, however, that the selection of certain useful models for testing does not in itself introduce any approximations into the treatment.

Typical results for some of the most relevant test models for the two sets of counter-diffractometer data are presented in Table 1. The table is arranged in order to facilitate direct comparison with the photographic data set considered in Ref. 2.

The final, but the most fundamental problem of the present study, is associated with the assessment of the relative correctness of the various models. As is commonly the case in crystallographic problems of this type it is difficult to design a suitable criterion for the comparison of the fitting of a large number of observed and calculated quantities.

Table 1. Positional parameters and temperature factors with standard deviations for different refinement models of FeS_2-*m*. Naturally shaped crystal: number of reflections 791. Spherically shaped crystal: number of reflections with $\sin \theta/\lambda \geqq 0.60$ is 610.

Crystal shape		Natural				Spherical	
Space group		*Pnnm*		*Pnn2*		*Pnnm*	*Pnn2*
Dispersion		Excl.	Incl.	Excl.	Incl.	Incl.	Incl.
Fe	β_{11}	0.00219(13)	0.00270(12)	0.00217(12)	0.00269(12)	0.00387(5)	0.00387(5)
	β_{22}	0.00166(7)	0.00199(7)	0.00167(7)	0.00200(7)	0.00238(3)	0.00238(3)
	β_{33}	0.00498(19)	0.00580(18)	0.00525(19)	0.00594(19)	0.00690(9)	0.00696(9)
	β_{12}	−0.00004(10)	−0.00001(10)	−0.00002(10)	−0.00002(10)	0.00007(6)	0.00007(6)
S	x	0.20040(14)	0.20052(14)	0.20051(14)	0.20054(14)	0.20008(6)	0.20001(7)
	y	0.37826(9)	0.37827(9)	0.37831(9)	0.37833(9)	0.37820(5)	0.37824(5)
	z	0	0	0.00441(48)	0.00163(45)	0	−0.00128(33)
	β_{11}	0.00365(16)	0.00366(16)	0.00367(16)	0.00369(16)	0.00456(7)	0.00456(7)
	β_{22}	0.00259(9)	0.00262(9)	0.00261(9)	0.00262(9)	0.00284(5)	0.00283(5)
	β_{33}	0.00733(25)	−0.00744(24)	−0.00711(27)	−0.00740(26)	−0.00805(12)	−0.00795(13)
	β_{12}	0.00098(18)	−0.00090(17)	−0.00087(17)	−0.00087(17)	−0.00051(9)	−0.00052(9)
	β_{13}	0	0	0.00425(87)	0.00369(85)	0	−0.00168(73)
	β_{23}	0	0	0.00283(63)	0.00246(65)	0	−0.00132(63)
	R	0.058_0	0.056_1	0.055_2	0.054_9	0.022_0	0.022_2
	R_w	0.079_7	0.076_3	0.076_5	0.074_8	0.025_2	0.024_8

An inherent, almost unsurmountable difficulty encountered in this connection is associated with the fact that crystallographic problems are generally non-linear and accordingly somewhat unsuitable for statistical treatments. The significance test of Hamilton [6] is the hitherto most widely accepted quantitative criterion for the kind of judgements which are to be performed. As is generally the case in statistics, the use of the Hamilton test is based on the supposition that there are no systematic errors in measurements, corrections, or computations (*vide supra*). Although there may be possible objections to the use of the Hamilton test, its unfailing correctness may be postulated for the present purpose. Hence, application of the test shows that the unrestrained model (Table 1) is superior to all the others at a significance level < 0.005 for each of the three data sets. Overlooking the distinction between statistical and physical significance, one may be led to the same inference on comparison of the values of the variable parameters with their associated standard deviations.

The superficial conclusion is accordingly that the mirror plane perpendicular to [001] at $z=\frac{1}{2}$ (and $z=0$) is missing in FeS_2-*m*, implying that *Pnn*2 is the correct space group for this compound. It is gratifying to note that this conclusion is identical with that drawn in Ref. 2. However, there appears to be a fundamental drawback attached to the findings in that on applying more refined and copious data, corrections, and computations the key parameter z_S gradually approaches zero. This finding is rather suspect and suggests very strongly that the mirror plane in question may be present in the structure of FeS_2-*m* despite the verdict based on the Hamilton test. The space group ambiguity for FeS_2-*m* is therefore not removed although the problem can be said to be on a rather different level from what it was when this project was started. The possible deviation of z_S from zero is now so small that no practical significance is attached to it. The principal cause of the difference between the present and preceding [2] study appears to be associated with the absorption correction. Similar considerations may apply to the data [1,2] for the isostructural compounds $FeSb_2$, $FeTe_2$, and $CoTe_2$.

It may be of interest to those who are entertaining the possibility of similar studies to summarize our practical experiences. In rough terms the improvement in R_w (and R) resulting from the more correct account for the absorption in the spherical crystal amounts to 4 to 5 times that obtained by the substitution of counter for photographic technique of intensity measurements. (It should be emphasized that both natural crystal fragments were of a particular unfavourable wedgeform for absorption according to the present computer programme.) The shift from film to counter detection is of equal importance to the removal of the undesirable low angle data ($\sin \theta/\lambda < 0.6$) from the calculations. Each of these means of improvement is in turn 4 to 5 times more important than the effects of dispersion. Altogether, the absorption correction turned out to be far more important than anticipated in advance.

In connection with the present redetermination of FeS_2-*m* it is of interest to summarize the development in the bonding Fe – S and S – S distances over the years:

	Fe – S(Å)	S – S(Å)
Buerger [8] (1931)	2.21 and 2.24	2.25
Buerger [9] (1937)	2.23_1 and 2.25_0	2.21_0

Brostigen and Kjekshus [2] (1971)	2.230(6), 2.235(2) and 2.275(6)	2.223(3)
Present (1973)	2.2359(3) and 2.2540(2)	2.2151(4)

(The uncertainties in the unit cell dimensions are not taken into account in the present values for the bond distances.) The figures clearly demonstrate the remarkable correctness of the bond distances provided by Buerger [9] in 1937.

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