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$Mn_{1-x}Fe_xS$, $x \simeq 0.05$, an example of an anti-wurtzite structure

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(Mn–S) = 0.001 Å
Disorder in main residue
R factor = 0.010
wR factor = 0.027
Data-to-parameter ratio = 13.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The mineral rambergite, hexagonal manganese sulfide, is found to crystallize in the inverse wurtzite structure, *i.e.* the wurtzite type structure but with the opposite absolute configuration, which can also be named anti-wurtzite. Rambergite was first found in the Garpenberg area, Dalarna, Sweden. The sample used in this investigation contained approximately 5% iron, as determined by microprobe analysis, giving the overall composition Mn_{1-x} Fe_x S, $x \simeq 0.05$.

Comment

The mineral rambergite, hexagonal MnS, was first found in the Garpenberg area, Dalarna, Sweden (Kalinowski, 1996). The name rambergite has been approved by the IMA Commission on New Minerals and Mineral Names. The manganese position in the Garpenberg sample is slightly substituted by other metals, mainly iron (5% in this particular sample), but also minor amounts of Sb, Zn and Ag were found by microprobe analysis of powder samples. The Fe content varied between 0.1% and 6% for different samples. No superstructure reflections could be detected, thus we assume negligible ordering of iron. The occurrence of rambergite has also been reported from Ronneburg, Thuringia, Germany (Witzke, 1999) without any indications of Fe substitution of the Mn position. In contrast to the wurtzite type structure, the present sample of rambergite crystallizes with the inverse absolute configuration. The inverted absolute configuration of wurtzite is equal to the anti-wurtzite model where the Mn and S atoms are swapped, such that the calculated structure-factor amplitudes are similar for the inverse wurtzite model and the anti-wurtzite model. This equality of the inverse wurtzite and the anti-wurtzite structure can be derived from traditional struc-

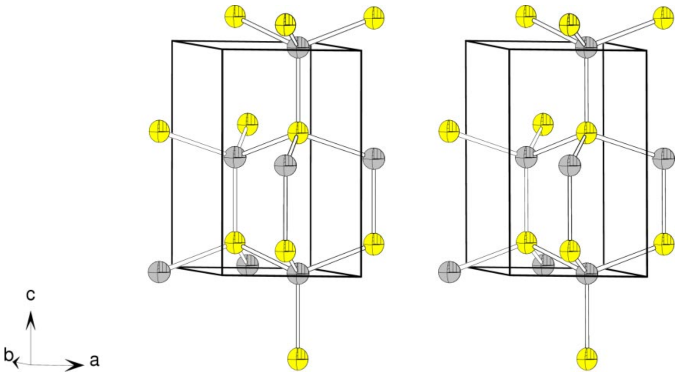

Figure 1
Stereoview of the rambergite structure with slightly more than the unit-cell content. Mn is grey and S yellow. Displacement ellipsoids are shown at the 90% level.

ture-factor formalism including anomalous dispersion corrections. Without the anomalous dispersion effects the wurtzite and anti-wurtzite structures are equal. It is not known if rambergite exists with the normal wurtzite absolute configuration. $c/a \simeq 1.619$ for rambergite and the value of $z(\mathrm{S}) = 0.6224$ (2), enabling the u-parameter of normal wurtzite to be calculated as $u = (1 - z) = 0.3776$ (2). These values fit very well in the (u, c/a) correlation scheme discussed for other wurtzite type structures, ZnS and ZnO (Kisi & Elcombe, 1989). The effect, concerning the parameter shifts, of changing the absolute configuration is rather small. It is of the order of 2σ when using the derived s.u.'s from the normal wurtzite model but increases when using the derived s.u.'s of the inverse wurtzite model. The derived s.u.'s of the parameters and derived quantities of the inverse wurtzite structure are generally smaller than the corresponding quantities for the normal wurtzite model. It is clear from comparison of R values and specially the Flack parameter for both the normal wurtzite model and the inverse wurtzite model, that the rambergite crystal should be of the inverse wurtzite structure type. Even though wurtzite is regarded as a simple structure, there is a definitive, however small, difference of the structure-factor expression for the wurtzite and anti-wurtzite structure due to anomalous dispersion corrections. Further investigations on several rambergite samples could be of interest to deduce the possibility for both absolute configurations to exist. The authors do not know of any multiple investigation of wurtzites with single-crystal methods in order to deduce the possibility of both absolute configurations. Many investigations on wurtzites have been performed with powder-diffraction data, but these are necessarily insufficient for determining absolute configuration. The physical factors that determine the absolute configuration of certain crystals is at present unclear. Some materials may be found with both absolute configurations; zinc hydroxide is one of these (Eriksson, 2001). Some important semiconductors, (Al,Ga,In)-nitrides, crystallize in the wurtzite structure. The effect of the polarity of the corresponding structures on electronic properties are, however, unknown to the authors.

Experimental

The sample is a naturally occurring mineral from Garpenberg, Dalarna, Sweden (Kalinowski, 1996) and has been given the name rambergite. No signs of superstructure reflections could be detected but a slight broadening of the reflections could be detected, perhaps due to the occurrence of concentration gradients.

Crystal data

$\mathrm{Fe_{0.05}Mn_{0.95}S}$
$M_r = 87.05$
Hexagonal, $P6_3mc$
$a = 3.982$ (2) Å
$c = 6.445$ (3) Å
$V = 88.49$ (8) Å^3
$Z = 2$
$D_x = 3.267$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 20.3$–$26.4°$
$\mu = 8.08$ mm^{-1}
$T = 293$ (2) K
Prism, dark brown
$0.22 \times 0.17 \times 0.13$ mm

Data collection

Stoe AED-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: numerical *X-RED* (Stoe, 1997)
$T_{\min} = 0.165$, $T_{\max} = 0.364$
546 measured reflections
78 independent reflections
72 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.037$
$\theta_{\max} = 24.8°$
$h = -4 \rightarrow 4$
$k = -4 \rightarrow 4$
$l = -7 \rightarrow 7$
3 standard reflections frequency: 120 min intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.010$
$wR(F^2) = 0.027$
$S = 1.05$
78 reflections
6 parameters
$w = 1/[\sigma^2(F_o^2) + (0.02P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.35$ e Å^{-3}
$\Delta\rho_{\min} = -0.34$ e Å^{-3}
Absolute structure: (Flack, 1983)
Flack parameter = 0.02 (4)

Table 1
Selected geometric parameters (Å, °).

Mn—S	2.4338 (16)	Mn—S$^{\rm i}$	2.4303 (12)
S—Mn—S$^{\rm i}$	108.93 (3)	S$^{\rm i}$—Mn—S$^{\rm ii}$	110.00 (3)

Symmetry codes: (i) $2 - x, 1 - y, \frac{1}{2} + z$; (ii) $1 - x, -y, \frac{1}{2} + z$.

The refinements with the wurtzite model gave clear indications that the inverse model was the correct one. The wurtzite model gave $wr2 = 0.084$, $R1(\text{all data}) = 0.032$ while the inverse wurtzite gave large improvements, $R1(\text{all data}) = 0.013$. The calculated Flack parameter was 1.0 (1) for the wurtzite model, thus clearly indicating the wrong absolute configuration. The z-coordinate of the mixed metal position was arbitrarily fixed at 1.0 in order for the model to be easily compared to other wurtzite type structures. At present it is unknown if both absolute configurations exist for rambergite, as only two single crystals of the mineral were available and unfortunately one of them was lost in the initial diffraction experiments. The iron content (5%) was determined by microprobe analyses. No attempt was made to deduce the iron content from refinements with the diffraction data. Iron and manganese are much too similar for this to be successful. The anisotropic displacement parameters for Fe and Mn were constrained to be equal in the least-squares calculations.

Data collection: *DIF*4 (Stoe, 1988); cell refinement: *DIF*4; data reduction: *X-RED* (Stoe, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Bergerhoff, 1996).

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