

X-ray and neutron diffraction study of the crystal structure of MnS_2

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Abstract. X-ray (293 K) and neutron diffraction (15 K, 67 K, 120 K, 293 K) intensities have been measured from natural single crystals of MnS_2 . The lattice parameter, interatomic distances and thermal parameters of Mn and S atoms vary approximately linearly in the temperature range from 15 K to 540 K. The mean volume thermal expansion coefficient is found to be $\beta = 3.70 \times 10^{-5} \text{ K}^{-1}$. The vibrational amplitudes of the Mn and S atoms are practically the same at 15 K but at 293 K the vibrational amplitude of the Mn atom becomes 25% larger than that of sulfur. The interatomic distances of MnS_2 have been compared with those of other pyrite-structure transition metal dichalcogenides and the nature of chemical bonding in these compounds has been discussed.

1. Introduction

Magnetic semiconductors MnX_2 ($\text{X} = \text{S}, \text{Se}, \text{Te}$) crystallize with the pyrite structure (cP12, space group $Pa\bar{3}$, C2-type) [1]. The Mn^{2+} ions in MnX_2 are in the high-spin state and carry magnetic moments corresponding to

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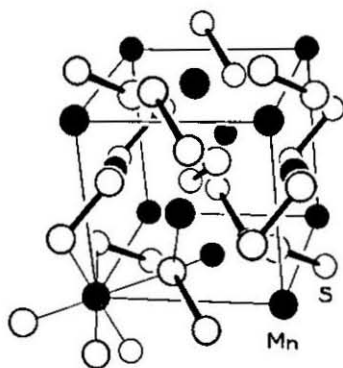


Fig. 1. Crystal structure of the pyrite-type MnS_2 .

five unpaired electrons. To understand the nature of chemical bonding in pyrite type compounds we have already performed accurate X-ray and neutron diffraction investigations on SiP_2 which is one of a few compounds of the main group elements that crystallize with the pyrite structure [2]. An accurate X-ray diffraction investigation has already been performed on the pyrite-type FeS_2 [3]. Although the mineral hauerite (MnS_2) is known to crystallize with the pyrite structure since 1930 [4], to our knowledge all structural investigations on MnS_2 are based on powder diffraction data [4–12]. In the present investigations we have performed X-ray and neutron diffraction measurements on *natural single crystals* of MnS_2 in the temperature range $15 \leq T(\text{K}) \leq 293$.

The pyrite structure and the closely related marcasite and arsenopyrite structure are exhibited by a very large number of compounds with compositions MX_2 , MY_2 or MXY where M is usually a transition metal and X, Y stand for 6B or 5B elements. These compounds have interesting and diverse electrical and magnetic properties [13, 14]. In these compounds the cations M are sixfold coordinated by distorted octahedra of anions whereas the anions X, Y are tetrahedrally (distorted) bonded to three M atoms and to one X or Y atom. Thus the structure contains covalent bonded pairs X_2 , Y_2 or XY (Fig. 1). The M–X bonds are different in character and are effected by the electronic state of M (high-spin, low-spin, p-element) and by the degree of ionicity. We have demonstrated this by Raman scattering [15] and we have shown that MnS_2 differs from FeS_2 and SiP_2 by the quasi-separation of M atoms and X_2 dumb-bells.

2. Experimental

We have used a natural crystal of MnS_2 (hauerite) of high purity, kindly supplied by Professor W. Hoffmann of the Institute of Mineralogy and

Crystallography, University of Münster, FRG. The large single crystal (octahedron with about 1 cm in linear dimensions) was cut to a smaller cube (4 mm $\times$ 4 mm $\times$ 4 mm) for neutron diffraction experiments. Two small pieces of the crystal one of size 0.06 mm $\times$ 0.06 mm $\times$ 0.026 mm and the other of a prismatic shape with linear dimensions of about 0.25 mm were used for X-ray diffraction. X-ray diffraction data have been measured at room temperature (293 K) with a Syntex P1 four-circle diffractometer using MoK_α radiation ($\lambda = 0.71069 \text{ \AA}$) up to $(\sin \theta/\lambda)_{\text{max}} = 1.2 \text{ \AA}^{-1}$. Neutron diffraction intensities have been measured at 15, 67, 120 and 293 K with the four-circle diffractometer D9 located at the hot neutron source at the high-flux reactor of the Institute Laue-Langevin, Grenoble. The low temperature at D9 was obtained by expanding compressed He gas through a nozzle in a closed cycle. The temperature was calibrated at the ferroelectric phase transition of a KH_2PO_4 single crystal at 122.5 K [16]. The measurements at 67 and 293 K were made with a neutron wavelength of $\lambda = 0.7002(3) \text{ \AA}$ and that at 120 K with $\lambda = 0.7096(2) \text{ \AA}$ using a conventional single detector. The lattice constant at each temperature was determined by refinement against the centered angles of 15 reflections. ω - 2θ scan mode was employed in bisecting geometry. The background of each reflection was estimated by the minimum $\sigma(I)/I$ method of Lehmann and Larsen [17]. The measurements at 15 K were made with a calibrated wavelength of $0.7049(2) \text{ \AA}$ and a small two-dimensional position-sensitive detector [18]. ω - $x\theta$ scan mode in bisecting geometry was employed with $x = x(\theta)$ chosen to keep the reflection at the centre of the detector. The background was subtracted using an extension of the $\sigma(I)/I$ method to three dimensions [19]. One advantage of a two-dimensional position-sensitive detector is that the centered angles of each reflection are also determined in the intensity measurement scan. Thus, the lattice constant at 15 K could be determined from the angles of all 329 strong and medium intensity reflections scanned. In addition, the variation in lattice constant from 300 K to 15 K could be conveniently followed by repeated scanning of 13 high-angle reflections at different temperatures. The intensity data were corrected for absorption (linear absorption coefficient $\mu = 0.094 \text{ cm}^{-1}$ and 73.60 cm^{-1} for neutron and X-rays, respectively).

3. Parameter refinement

Full matrix least-squares refinements of the structure were performed with the X-RAY 72 program system. The refined parameters and the interatomic distances are given in Table 1. Neutron scattering lengths used for Mn and S atoms were $-3.73 \times 10^{-13} \text{ cm}$ and $2.847 \times 10^{-13} \text{ cm}$, respectively [20]. X-ray scattering factors were taken from reference [21].

Table 1. Temperature dependence of the crystal structure of MnS_2 (Space group $Pa\bar{3}$, $Z = 4$, Mn at 4(a) 000 and S at 8(c) xxx, $U_{11} = U_{22} = U_{33}$, $U_{12} = U_{13} = U_{23}$).

	Neutron 15 K	Neutron 67 K	Neutron 120 K	Neutron 293 K	X-ray I 293 K	X-ray II 293 K
a (Å)	6.083(2)	6.087(2)	6.091(2)	6.104(2)	6.104(2)	6.104(2)
Mn: x	0	0	0	0	0	0
U_{11} (Å ²)	0.00139(4)	0.0035(2)	0.0048(2)	0.0100(2)	0.01152(6)	0.0105(1)
U_{12} (Å ²)	0.00003(4)	0.00024(8)	0.00012(8)	0.0005(1)	0.00023(7)	0.0005(1)
S: x	0.40078(4)	0.40106(6)	0.40090(5)	0.40108(5)	0.40107(4)	0.40121(7)
U_{11} (Å ²)	0.00147(4)	0.0029(2)	0.0040(2)	0.0079(2)	0.00910(7)	0.0082(1)
U_{12} (Å ²)	0.00004(7)	0.0004(8)	0.00026(1)	0.00062(8)	0.00038(7)	0.0004(1)
$N(hkl)$	260	359	364	369	517	358
R	0.026	0.026	0.021	0.025	0.051	0.034
$d(\text{Mn}-\text{Mn})$ (Å)	4.301(1)	4.304(1)	4.307(1)	4.316(1)	4.316(1)	4.316(1)
$d(\text{Mn}-\text{S})$ (Å)	2.5830(8)	2.5856(8)	2.5868(8)	2.5928(8)	2.5928(8)	2.5932(9)
$d(\text{S}-\text{S})$ (Å)	2.0908(6)	2.0862(8)	2.0910(7)	2.0917(7)	2.0919(6)	2.0889(9)

$N(hkl)$ = number of independent reflections.

$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$, F_o = observed structure factor, F_c = calculated structure factor.

Table 2. Lattice parameter and interatomic distances in the pyrite type metal disulfides MS_2 ($M = \text{Mn, Fe, Co, Ni, Cu, Zn}$).

	MnS_2	FeS_2 [27]	CoS_2 [28]	NiS_2 [28]	CuS_2 [26]	ZnS_2 [1]
formal 3d electron configuration	$d^5(t_{2g})^3(e_g)^2$	$d^6(t_{2g})^6$	$d^7(t_{2g})^6(e_g)^1$	$d^8(t_{2g})^6(e_g)^2$	$d^9(t_{2g})^6(e_g)^3$	$d^{10}(t_{2g})^6(e_g)^4$
a (Å)	6.104	5.4175	5.5385	5.6865	5.7891	5.9542
$d(\text{S}-\text{S})$ (Å)	2.091	2.177	2.113	2.072	2.030	—
$d(\text{M}-\text{S})$ (Å)	2.593	2.262	2.325	2.399	2.453	—
$d(\text{M}-\text{M})$ (Å)	4.316	3.831	3.916	4.021	4.094	4.210

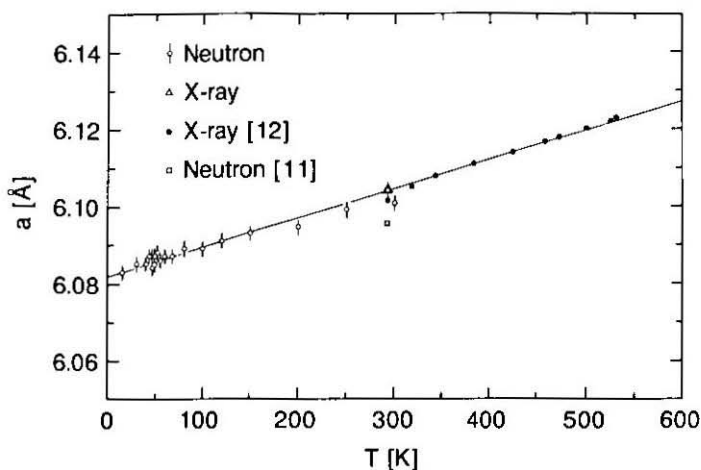


Fig. 2. Temperature variation of the lattice parameter of MnS_2 . High temperature lattice parameters determined by Furuseth and Kjekshus [12] from X-ray powder photographs and the room temperature neutron powder data of Hastings et al. [11] are also shown.

After comparing the observed and calculated structure factors for all the data, we were convinced that no serious extinction effects were present. We have therefore not attempted any extinction correction. A careful examination of the intensity data did not reveal the presence of multiple scattering. No correction to the intensity data due to the thermal diffuse scattering (TDS) has been attempted because of the lack of information about the phonon dispersion in MnS_2 . The above mentioned correction factors which have been neglected in the present refinements must be small and this is reflected in the good agreement factors.

4. Results and discussion

4.1. Lattice parameter

Figure 2 shows the lattice parameter a as a function of temperature along with the high temperature data of Furuseth and Kjekshus [12], obtained from X-ray powder photographs of synthetic MnS_2 and the room temperature neutron data of Hastings et al. [11]. The data of Furuseth and Kjekshus [12] have less standard deviations than our measurements. The present neutron single crystal determination was performed at different times with different monochromator settings, leading to uncertainty in the value of the neutron wavelength. However, the low temperature data fit very well the almost linear behaviour of the high temperature data of Furuseth and

Kjekshus [12] (Figure 2) which also includes our X-ray single crystal value. It cannot be excluded that there are small differences in the lattice parameter of natural and synthetic MnS_2 . Nevertheless, all data fulfill with high precision ($\pm 0.001 \text{ \AA}$) the linear relationship $a = a_0 + \alpha^* T$ with $a_0 = 6.0818 \text{ \AA}$ and $\alpha^* = 7.52 \cdot 10^{-5} \text{ \AA} \cdot \text{K}^{-1}$. Larger deviations occur only with our room temperature neutron diffraction value and with the value given by Hastings et al. [11]. The average linear thermal expansion coefficient $\alpha = a^{-1} (\Delta a / \Delta T) = 1.23 \cdot 10^{-5} \text{ K}^{-1}$ corresponds to the volume thermal expansion coefficient $\beta = 3\alpha = V^{-1} (\Delta V / \Delta T) = 3.70 \cdot 10^{-5} \text{ K}^{-1}$. Thus, the thermal expansion coefficient of MnS_2 is considerably larger than that of FeS_2 measured by Straumanis et al. [22] ($\alpha = 0.925 \cdot 10^{-5} \text{ K}^{-1}$; $\beta = 2.78 \cdot 10^{-5} \text{ K}^{-1}$). This behaviour corresponds with the compressibility of MnS_2 which is also larger than that of pyrite-type p- FeS_2 ($1.32 \cdot 10^{-3} \text{ kbar}^{-1}$ [23] $\geq 0.68 \cdot 10^{-3} \text{ kbar}^{-1}$ [23]). This is obviously related to the high spin state of Mn^{2+} in MnS_2 (see below).

4.2. Interatomic distances

The interatomic distances are given by the positional parameter $x(\text{S})$ which seems to be highly accurate by the refinements, but also by the lattice parameter which at least increase the error in e.g., the S—S distance up to $\pm 0.001 \text{ \AA}$ by their large standard deviations (Table 1). Therefore we have chosen the more probable lattice parameters calculated from the linear relationship given above: **15 K**, $a = 6.083(2) \text{ \AA}$, $x = 0.40078(4)$; **67 K**, $a = 6.087(2) \text{ \AA}$, $x = 0.40106(6)$; **120 K**, $a = 6.091(2) \text{ \AA}$, $x = 0.40090(5)$; **293 K**, $a = 6.104(2) \text{ \AA}$, $x = 0.40108(5)$.

We would like to point out that at 293 K, the bond distance $d(\text{S}—\text{S})$ shows small differences in the three independent refinements (Table 1). The mean value $2.0908(17) \pm 2.091(2) \text{ \AA}$ of all three determinations has a larger standard deviation than the single values. This is affected by the second X-ray determination.

Figure 3 shows the temperature variation of the interatomic distances. The Mn—Mn and Mn—S distances vary approximately linearly, whereas the S—S distance practically remains constant (as with NiS_2 [28]), except for the 67 K value. Including all data yield an increase with temperature which is about 10% of that of the other distances ($d(\text{S}—\text{S}) = 2.0889 + 6.35 \times 10^{-6} T$). We are not sure if the 67 K value is an artifact or not, but this effect may be related to the onset of the antiferromagnetic ordering at about 48 K [24]. The general temperature variation corresponds to the stronger covalent bond within the S_2 dumb-bells and relatively weak Mn—S bonds whose character is dominantly ionic with small covalent contribution. These results are consistent with those of Raman scattering investigation of MnS_2 [15] in which a clear separation of stretching and librational frequencies, small Davydov splitting and strong overtone at exactly twice

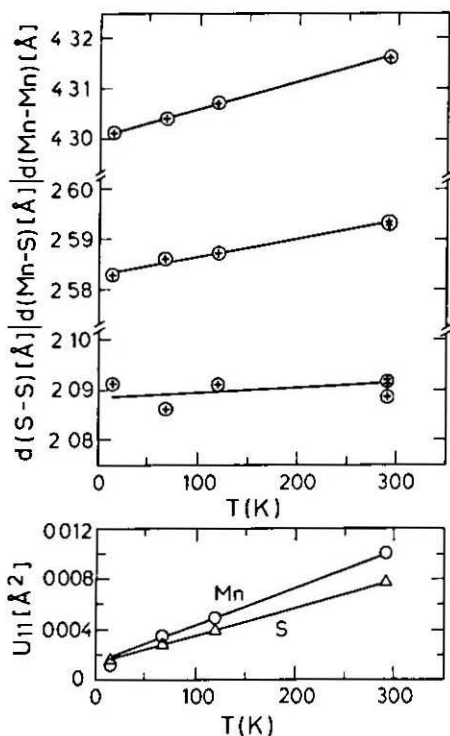


Fig. 3. (above): Temperature variation of the interatomic distances of MnS_2 obtained from single crystal neutron diffraction data (for $d(\text{S-S})$ at 67 K cf. text). (below): Temperature variation of the thermal parameter U_{ij} of Mn and S atoms in MnS_2 . The off-diagonal terms $U_{12} = U_{13} = U_{23}$ are found to be practically zero.

the stretching mode frequency indicate that the concept of quasi isolated dumb-bell S_2 units can be approximately applied to MnS_2 , at least better than for FeS_2 and SiP_2 . However, quantum chemical calculations show [25] that the appropriate bond distance in a really isolated S_2^{2-} anion is expected to be as large as $d(\text{S-S}) = 2.2020 \text{ \AA}$. Therefore, even in MnS_2 ($d(\text{S-S}) = 2.091 \text{ \AA}$) the covalent back-bonding contribution is not really negligible. Figure 3 also shows the temperature variation of the thermal parameter $U = U_{11} = U_{22} = U_{33}$ of Mn and S atoms. At low temperature U is practically the same for Mn and S atoms whereas at room temperature $U(\text{Mn})$ is larger than $U(\text{S})$ by about 25%. This is again what is expected for strong covalently bonded S_2 dumb-bells. The thermal parameters obtained from the X-ray data are higher than those obtained from neutron data because the X-rays are diffracted from both core and non-spherical valence electrons.

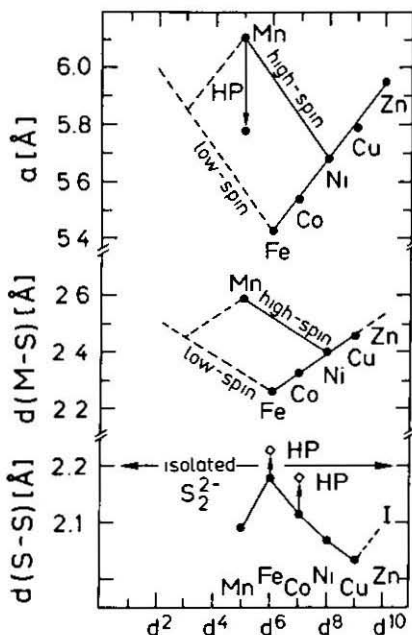


Fig. 4. Variation of the lattice parameter and interatomic distances of the series of pyrite-structure compounds MS_2 ($M = \text{Mn, Fe, Co, Ni, Cu, Zn}$). The high pressure data (HP) for FeS_2 and CoS_2 [31] are fitted to the zero pressure bond length for comparison (cf. [32]). The S-S bond length of ZnS_2 is estimated.

In Table 2 we compare the lattice parameter and interatomic distances of the pyrite type series compounds MS_2 ($M = \text{Mn, Fe, Co, Ni, Cu, Zn}$) with d^5-d^{10} electronic configuration [1, 26, 27, 28]. Figure 4 shows the variation of lattice parameters, S-S and M-S distances as functions of the number of d electrons. The variation of the distances reflect the different electronic states (high-spin; low-spin) and was already discussed by Kjekshus and Nicholson [29]. The extrapolated volume for a low-spin MnS_2 -p should be about 24% less than that of the high-spin MnS_2 -p. At about 140 kbar a first-order phase transition occurs to a marcasite type MnS_2 -m [23] with a volume contraction of about 15%. As the volumes of marcasites and corresponding pyrites have ratios of about 1.03–1.07 [1] this contraction is comparable with a high-spin to low-spin transition. The steady increase in M-S distance by going from the metal electronic state low-spin d^6 , through low-spin d^7 to d^8 results from an increasing number of electrons entering into anti-bonding e_g^* bands. That weakens the M-S bond and consequently the X-X bond strength is increased (Fig. 4). High-spin MnS_2 has a shorter S-S bond distance (2.091 Å) compared to that for the low-spin FeS_2 (2.177 Å).

Takéuchi et al. [30] determined the S—S bond distance in CuS as a function of hydrostatic pressure, and have found this distance to increase with pressure from 2.086(7) Å at 1 bar to 2.44(20) Å at 33 kbar. Similar results were obtained by Will et al. [31] on FeS_2 and CoS_2 . By means of synchrotron X-ray powder diffraction they found that the S—S bonds of the S_2 groups of FeS_2 and CoS_2 are lengthened with an increase of pressure. For CoS_2 the S—S bond distance increases from 2.17(2) Å at $P = 0$ kbar to 2.24(2) Å at 32.5 kbar. For FeS_2 the S—S bond distance increases from 2.14(4) Å at $P = 0$ kbar to 2.19(4) Å at $P = 38.5$ kbar [32]. Will et al. [31] do not give an interpretation of this result, whereas Takéuchi et al. [30] suggest that pressure probably induces delocalization of the electrons in the S_2 groups. We consider this interpretation to be essentially correct. Application of pressure induces charge transfer from the metal atom to the antibonding electronic states of the S_2 unit, causing a weakening of the S—S bond and its consequent lengthening.

The chemical bonding in pyrite-structure compounds and the closely related marcasite and arsenopyrite-type compounds have been discussed by several authors [13, 14, 27, 29, 33–39] and the electronic band structure of the series MS_2 ($M = \text{Fe, Co, Ni, Cu, Zn}$) have been calculated [40–42]. However, the band structure of the magnetic semiconductor MnX_2 ($X = \text{S, Se, Te}$) have not been reported. The structures belong to a general family of MX_2 compounds in which X_2 dimers have different orientations. These structures can be derived from the CaC_2 structure by dimer tilting, X—X bond breaking and M—X bond breaking. These processes have been beautifully illustrated by Burdett and McLarnan [37]. Band structure calculations of these authors by using the extended Hückel approach, support the above mentioned crystal chemical arguments.

In progressing across the disulfide series from MnS_2 to ZnS_2 , electrons are progressively added to the cation d orbital set. The diverse electrical and magnetic properties of this series can be explained in terms of the localized versus delocalized behaviour of electrons in the dominantly cation $3d$ type orbitals. Electrons in the t_{2g} π -type orbitals remain localized on the cation, whereas the overlap of e_g type orbitals on adjacent metals via S atoms leads to the formation of the e_g^* band. In the semiconductor MnS_2 three d electrons go to the t_{2g} levels, whereas 2 electrons go to the e_g^* band, forming a high-spin state. The e_g^* band is completely empty in the diamagnetic semiconductor FeS_2 (low-spin state). In the metallic phases CoS_2 and CuS_2 , the e_g^* band is partially filled, and in the diamagnetic insulator ZnS_2 it is completely filled. In NiS_2 spin splitting of electrons in these orbitals is sufficient to split the e_g^* band into a filled and empty band, leading to semiconducting properties and ordered magnetism.

The present X-ray and neutron diffraction intensity data of MnS_2 single crystals have led to accurate structural parameters consistent with chemical bonding and also with the results of Raman scattering [15] and high pressure

X-ray diffraction measurements [23]. However, attempts to determine valence electron density distributions of MnS_2 from these data were less successful. The deformation densities $\rho_{\text{X-X}}$ and $\rho_{\text{X-N}}$ show weak bonding electron density (maximum value = $0.2 \text{ e}/\text{\AA}^{-3}$) at the center of the S—S bond [33]. The bonding electron density in the Mn—S bond is found to be very diffuse, but this effect may be due to the more ionic behavior of MnS_2 with a highly charged S_2^{2-} unit.

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