On the Bonding in Tetragonal FeS

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[57]Fe Mössbauer spectroscopic data for tetragonal iron monosulphide
give a chemical shift of $0.62-0.63$ mm/s relative to sodium nitro-
prusside, a line width of $0.38-0.41$ mm/s, and a non-resolvable
quadrupole splitting. These results are discussed in terms of a tentative
bonding scheme for the compound.

Mackinawite (an iron sulphide mineral first described by Evans *et al.*[1,2]) was shown by Berner [3,4] to be identical with a synthetic tetragonal modification of iron monosulphide. The composition of this mineral is apparently nearly stoichiometric, but about 15 % of the iron atoms are often found to be substituted by Ni, Co, and/or Cu. Although the composition of mackinawite was originally given with a metal to sulphur ratio of unity, most chemical analyses (*cf.*, *e.g.*, Refs. 5 and 6) show a slight excess of metal and its formula is usually presented as $Fe_{1+x}S$ where Fe represents the sum of Fe, Ni, Co, and Cu, and $0.04 \leq x \leq 0.07$ [5] or $0.01 \leq x \leq 0.08$.[7]

The analogous phases of the $Fe-Se$ [8] and $Fe-Te$ [9] systems also appear to be stabilized by an excess of Fe according to a formula $Fe_{1+x}Y$ ($Y = S$, Se, or Te), where x increases on going from S to Te. However, any deviation in stoichiometry is of subordinate importance in the present context and also, in order to avoid the more complicated formula $Fe_{1+x}S$, the notation FeS-*t* (t = tetragonal) will be used throughout this paper.

As a result of X-ray [4,10—13] and neutron [11] diffraction studies FeS-*t* has been assigned the anti-PbO type structure (Fig. 1). The evidences from the neutron diffraction and Mössbauer data by Bertaut *et al.*[11] demonstrate that there is no cooperative magnetism present in this phase above 1.7 K. Morice *et al.*[14] have on the other hand published Mössbauer data which contradict this finding. The Mössbauer spectrum for FeS-*t* reported by the latter authors consists of several overlapping hyperfine patterns. In order to resolve this ambiguity a redetermination of the Mössbauer parameters for FeS-*t* was undertaken.
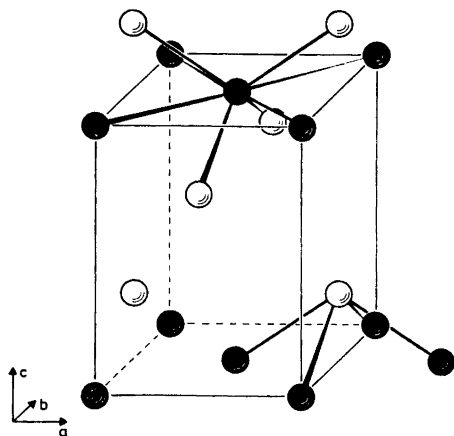
Fig. 1. The anti-PbO type structure of FeS-*t*. Filled and open circles represent iron and sulphur atoms, respectively.

EXPERIMENTAL

Following the procedure of Berner[4] turnings from iron rods (spectroscopically standardized, Johnson, Matthey & Co.) were placed in an aqueous solution of sodium sulphide which was deaerated by bubbling nitrogen through the boiling solution. The pH was adjusted to ~ 5 by the addition of an acetic acid/sodium acetate buffer. The black sulphide which formed after several days (under nitrogen atmosphere) was filtered off, washed several times with deaerated water, and finally with acetone.

X-Ray powder data were recorded on a Siemens diffractometer using Ni-filtered CuKα-radiation. Additional X-ray data were collected with an 80 mm diameter Guinier type camera and monochromatized CuKα_1-radiation ($\lambda = 1.54050$ Å). KCl ($a = 6.2919$ Å[15]) was used as an internal standard in both cases. The unit cell dimensions were determined by applying the method of least squares. The error limits stated in the text correspond to the standard deviations obtained in these calculations.

The samples for the Mössbauer spectroscopic measurements contained ~ 25 mg Fe per cm^2 absorber area. Discs of thickness 2 mm were prepared by mixing the specimen with "Specifix" cold mounting resin from Struers. This technique of absorber preparation results in the sample being homogeneously dispersed and has the added advantage of protecting the sulphide from the atmosphere. Both the absorber and the source (5 mCi ^{57}Co in a Pd matrix) were kept at room temperature. The source motion was provided by a Nuclear Science & Engineering Corporation model NS-1 spectrometer operating in the constant acceleration mode. The γ-ray detector was of the NaI(Tl) scintillator type. The data were recorded on 400 channels of a PIP 400 Victoreen pulse height and multichannel analyser. Calibrations with a sodium nitroprusside absorber were performed before and after each experiment. The source and the sodium nitroprusside standard were obtained from the U.K.A.E.A. Radiochemical Centre, Amersham, United Kingdom.

RESULTS AND DISCUSSION

The present samples were identified as single phase FeS-*t* according to the X-ray powder diffraction data (*viz.* the relative intensities of the reflections as well as the deduced unit cell dimensions $a = 3.684(2)$ Å, $c = 5.041(3)$ Å, $c/a = 1.368(2)$) which are in good agreement with those reported earlier.[4,10-13]

Fig. 2 shows a typical example of our Mössbauer spectra of FeS-*t*. The parameters extracted from this and other spectra are chemical shifts (δ)
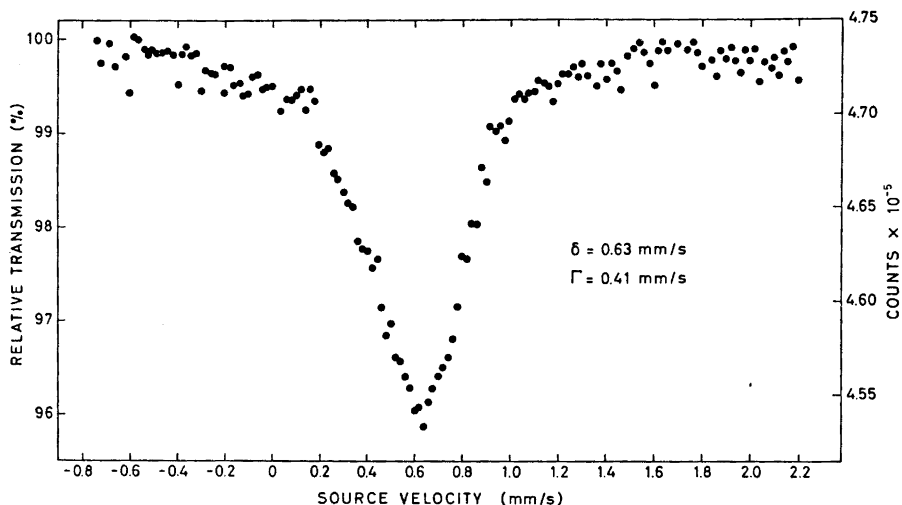
Fig. 2. [57]Fe Mössbauer spectrum of FeS-*t* at 300 K.

ranging between 0.62 and 0.63 mm/s and line-widths (Γ) from 0.38 to 0.41 mm/s. These results compare well with the data presented by Bertaut *et al.*[11] ($\delta = 0.61$ mm/s), but differ markedly from those of Morice *et al.*[14] The latter authors did not include phase analytical data, but considering the Mössbauer spectra presented in their Fig. 1 the most natural inference is that their FeS-*t* sample contained considerable amounts of other iron sulphide phases.

The interpretation of these findings is conveniently made in terms of the chemical bonding scheme suggested for the compound. As seen from Fig. 1, the orbital arrangement for the sulphur atoms may be described as a square pyramid with the apex vacant. Thus the symmetry of this polyhedron is approximately that of point group C_{4v}. a_1, e, and b_2 symmetry orbitals are directed from the sulphur atom within the pyramid towards the four corners at the base and a fifth orbital of a_1 symmetry, occupied by an unshared electron pair, is directed towards the apex.

The interatomic Fe – S distance of 2.23 Å in FeS-*t* may be compared with the representative Fe – S bond lengths listed by de Médicis.[16] (This paper unfortunately contains a misprint with respect to the Fe – S distance in FeS-*t*.) Except possibly for iron sulphides belonging to the NiAs family, all the other compounds considered by de Médicis possess covalent properties, including FeS-*t*. Unlike the high-spin compounds treated by de Médicis, FeS-*t* contains low-spin iron according to the magnetic and Mössbauer spectroscopic data (*vide supra* and Ref. 11). The short Fe – S bond length for this compound may be ascribed in part to the smaller radius of low-spin Fe as compared with the high-spin case.[17]

The iron atoms in FeS-*t* are tetrahedrally bonded to four sulphur atoms (Fig. 1). This arrangement may be compared with that of the metal atoms in chalcopyrite ($CuFeS_2$), sphalerite ($(Fe,Zn)S$), and stannite (Cu_2FeSnS_4).

These compounds take the zinc blende type structure, in which the metal atoms are tetrahedrally coordinated by sulphur atoms, and *vice versa*. Structural,[18-20] electrical,[21] magnetic,[20,21] and Mössbauer spectroscopic[22] studies have been performed on chalcopyrite, and all available data suggest a covalent type of bonding for this substance. Similarly, a covalent model appears to apply to sphalerite and stannite (*cf., e.g.*, Refs. 22 and 23). The formal valences correspond to Fe(III) for chalcopyrite and Fe(II) for sphalerite and stannite. These valences are a consequence of the distribution of six valence electrons from sulphur among four saturated tetrahedral bonds. The hypothetical bonding scheme for chalcopyrite presented in Fig. 3 is consistent with the
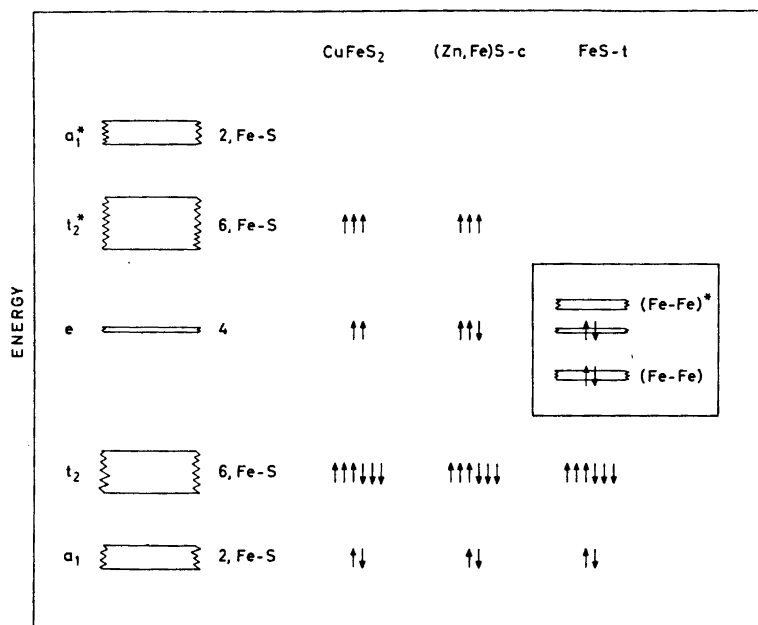

Fig. 3. Hypothetical energy band diagrams for chalcopyrite ($CuFeS_2$), sphalerite ((Zn,Fe)S), and FeS-*t*. The filling of the Fe$-$S and Fe$-$Fe bands is indicated by the arrows.

electron configurations d^{10} and high-spin d^5 on Cu(I) and Fe(III), respectively.[20] Similarly, the iron atoms in stannite and sphalerite, which receive a share in a total of six sulphur electrons, obtain a high-spin d^6 configuration (Fig. 3).

The bonding situation in FeS-*t* requires two important modifications to the scheme for chalcopyrite, sphalerite, and stannite, the changes being imposed by structural differences. Firstly, the sulphur atoms in FeS-*t* distribute their electrons among five orbitals (four bonding and one nonbonding). The assumption that each Fe$-$S bond is saturated by an electron pair implies a d^4 configuration for Fe. Secondly, the short interatomic Fe$-$Fe distance of 2.60 Å definitely implies that there is bonding interaction between the metal atoms. According to the structure there is a square planar network of

Fe−Fe bonds in FeS-t. This bonding situation may be visualized as arising from the overlap of (say) the $d_{x^2-y^2}$ orbitals on one iron atom with the corresponding orbitals on its four nearest iron neighbours. Hence, the bonding $d_{x^2-y^2}$ orbital is lowered in energy relative to the nonbonding d_{z^2} orbital as indicated in Fig. 3. This explains the absence of a magnetic moment in FeS-t.

In considering the value of δ for FeS-t it would have been of considerable interest to compare this value with those for the isostructural iron selenide and telluride phases. Although Mössbauer spectroscopic data for the $Fe_{1.11}Te$ phase have been published by Suwalski et al.[24] direct comparison of δ-values is made difficult by the uncertainty concerning the standard used in their study of the telluride.

The low-spin configuration of the iron atoms in FeS-t causes δ to be somewhat insensitive to the oxidation state, whereas the chemical shifts for the high-spin Fe(II) and Fe(III) sites in (Zn,Fe)S and $CuFeS_2$ are much more sensitive to differences in their electronic configurations ($\delta = 0.95$ [23] and 0.49 mm/s,[22] respectively). Also, the extent to which the metal d-electrons are delocalized over the molecular framework of these covalent compounds influences the shielding of the iron nuclei from the s-electron density. This delocalization is three-dimensional in chalcopyrite, sphalerite, and stannite, but is largely two-dimensional in FeS-t in which the delocalized electron density is restricted to the network of iron atoms.

Contributions to quadrupole interaction in FeS-t arise from three major sources. Firstly, there is an imbalance in the occupation of the nonbonding or antibonding $3d$ orbitals consequent on the lifted degeneracy of the e-type orbitals (Fig. 3) which in turn is a result of the Fe−Fe bonding. Secondly, the deviation from cubic symmetry of the tetrahedral Fe−S bonds results in electron imbalance. Finally, there is the polarizing effect due to the lattice, which is, however, presumably quite small in the case of FeS-t.

The absence of a resolvable quadrupole interaction in FeS-t is open to interpretation. It is worth noting that a small quadrupole splitting ($\Delta = 0.26$ mm/s at 298 K) has been observed for the isostructural telluride.[24] Naively, the absence of a quadrupole interaction in FeS-t may be attributed to a net cancellation of the various terms which contribute to the electric field gradient, i.e. resulting in an apparent cubic symmetry of the electronic charge distribution around the iron nuclei. A quantitative evaluation of the various contributions to the total electric field gradient is clearly impossible, which in part is a consequence of the fact that the Fe−Fe bonding most probably is of the delocalized "metallic" type.

REFERENCES

1. Evans, H. T., Berner, R. A. and Milton, C. Geol. Soc. America, Annual Meeting 1962, p. 47.
2. Evans, H. T., Milton, C., Chao, E. C. T., Adler, I., Mead, C., Ingram, B. and Berner, R. A. U. S. Geol. Surv. Profess. Papers 475 D 1964, p. D64.

3. Berner, R. A. *Science* **137** (1962) 669.
4. Berner, R. A. *J. Geol.* **72** (1964) 293.
5. Takeno, S. and Clark, A. H. *J. Sci. Hiroshima Univ. Ser. C* **5** (1967) 287.
6. Springer, G. *Neues Jahrb. Mineral., Monatsh.* **8** (1968) 252.
7. Mukherjee, A. D. *To be published.*
8. Grønvold, F. and Westrum, E. F. *Acta Chem. Scand.* **13** (1959) 241.
9. Westrum, E. F., Chou, C. and Grønvold, F. *J. Chem. Phys.* **30** (1959) 761.
10. Kouvo, O., Vuorelainen, Y. and Long, J. V. P. *Am. Mineralogist* **48** (1963) 511.
11. Bertaut, E. F., Burlet, P. and Chappert, J. *Solid State Commun.* **3** (1965) 335.
12. Uda, M. *Z. anorg. allgem. Chem.* **361** (1968) 94.
13. Taylor, L. A. and Finger, L. W. *Carnegie Institution Year Book* **1969 – 70** 318.
14. Morice, J. A., Rees, L. V. C. and Rickard, D. T. *J. Inorg. Nucl. Chem.* **31** (1969) 3797.
15. Hambling, P. G. *Acta Cryst.* **6** (1953) 98.
16. de Médicis, R. *Rev. Chim. Minér.* **7** (1970) 723.
17. Kjekshus, A. and Nicholson, D. G. *Acta Chem. Scand.* **25** (1971) 866.
18. Pauling, L. and Brockway, L. O. *Z. Krist.* **82** (1932) 188.
19. Boon, J. W. *Rec. Trav. Chim.* **63** (1944) 69.
20. Donnay, G., Corliss, L. M., Donnay, J. D. H., Elliott, N. and Hastings, J. M. *Phys. Rev.* **112** (1958) 1917.
21. Teranishi, T. *J. Phys. Soc. Japan* **16** (1962) 1881.
22. Greenwood, N. N. and Whitfield, H. J. *J. Chem. Soc.* **A 1968** 1697.
23. Marfunin, A. S. and Mkrtchyan, A. R. *Geochem. Internat.* **4** (1967) 980.
24. Suwalski, J., Piekoszewski, J. and Leciejewicz, J. *J. Phys. Soc. Japan* **26** (1969) 1546.