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On the Bonding in Berthierite ($FeSb_2S_4$)

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Magnetic susceptibility and ^{57}Fe and ^{121}Sb Mössbauer spectroscopic data for the mineral berthierite ($FeSb_2S_4$) are reported and discussed in relation to its crystal structure. The Fe atoms are in a high-spin d^6 state and the bonding is considered to be predominantly covalent in this compound.

The crystal structure of berthierite ($FeSb_2S_4$) as determined by Buerger and Hahn [1,2] does not appear to have received much attention apart from a few references in the mineralogical literature. This is somewhat surprising in view of the bonding implications which appear to follow from this particular structural arrangement.

$FeSb_2S_4$ contains two favourable Mössbauer nuclei, *viz.* ^{57}Fe and ^{121}Sb, and it is therefore tempting to subject this compound to Mössbauer spectroscopic studies. Marfunin and Mkrtchyan [3] have, in fact, already reported ^{57}Fe Mössbauer data for berthierite. Magnetic susceptibility measurements on the compound are, moreover, desirable in order to verify unambiguously the spin state of the Fe atoms.

EXPERIMENTAL

The natural berthierite sample used in this study originated from Ringvassøy, Norway. The original sample was crushed and the 140 – 200 mesh particle size fraction selected. Berthierite was separated from associated quartz by repeated heavy liquid and magnetic separations. The identity and homogeneity of the resulting sample was ascertained both microscopically and from Guinier photographs.

The experimental details concerning the X-ray diffraction, ^{57}Fe and ^{121}Sb Mössbauer, and magnetic susceptibility measurements have been presented in previous communications.[4–6]

RESULTS AND DISCUSSION

The X-ray diffraction data for the present mineral sample unambiguously identify it as berthierite ($FeSb_2S_4$). The unit cell dimensions $a = 11.407(2)$ Å,

$b = 14.159(2)$ Å, $c = 3.7602(5)$ Å are consistent with those found by Buerger and Hahn.[2]

The structure determination reported by the latter authors gives the geometry of the atomic arrangement and interatomic distances accurate to about 0.02 Å, which is quite adequate for discussion on the bonding in $FeSb_2S_4$. The structure consists of one kind of Fe site and two and four crystallographically non-equivalent sites for Sb and S, respectively. The Fe atoms are surrounded by six S atoms in a distorted octahedral arrangement (Fe – S ranging from 2.45 to 2.64 Å, with a weighted average of 2.53 Å). Each kind of Sb atoms is bonded to three S atoms (the weighted averages for the $Sb_I - S$ and $Sb_{II} - S$ bond lengths are 2.46 and 2.54 Å, respectively).

Considering bonding interactions as being significant only between the nearest neighbours, *viz.* Fe to S and Sb to S, the valence states of the various kinds of atom are deduced to be Fe(II), Sb(III), and S(II). The same conclusion is reached in terms of the generalized (8 – N) rule (*cf.*, *e.g.*, Ref. 7):

$$n + P - Q = 8 \cdot a$$

where the use of the figure 8 is justified by the fact that the non-metal atoms obtain formally complete octets, and (per formula unit) a is the number of non-metal atoms, n the total number of bonding electrons, and P and Q, respectively, the number of electrons engaged in non-metal – non-metal and metal – metal bonds. With $a = 2 + 4 = 6$, $n = 2 + 2 \times 5 + 4 \times 6 = 36$, $P = 12$, and $Q = 0$ the rule is satisfied for $FeSb_2S_4$.

The nearest neighbour Fe – S distances are assumed to represent single bonds in the above considerations. A comparison of the average Fe – S bond length in $FeSb_2S_4$ with the corresponding distances in other octahedrally coordinated iron sulphides suggests that the Fe atoms in $FeSb_2S_4$ are in the high-spin d^6 state. A recent example of high-spin Fe(II) is given by Bargeron *et al.*[8] on the basis of ^{57}Fe Mössbauer studies on small amounts of Fe in MnS_2 which takes the FeS_2-pyrite type structure (Fe – S bond length 2.592 Å[9]). The correspondence between bond length and spin state is nicely demonstrated by contrasting this situation with that in FeS_2-pyrite itself (Fe – S bond length 2.262 Å;[9] low-spin Fe(II)).

The temperature dependence of the reciprocal magnetic susceptibility of $FeSb_2S_4$ obeys the Curie-Weiss Law $\chi^{-1} = C^{-1}(T - \theta)$ over the range 80 to 650 K. (The upper temperature limit gives the approximate melting/decomposition point.) A least squares fit of the experimental data gives $\theta = 175 \pm 25$ K and $\mu_P = \sqrt{8C_{mol}} = 5.0 \pm 0.1$ μ_B; the corresponding spin quantum number according to the "spin only" approximation is $2S_{Fe} = 4.1 \pm 0.1$ as required for high-spin d^6. There is no indication of a cooperative magnetic phenomenon above 80 K. This finding is consistent with the low value of θ and is, moreover, not unexpected in view of the large Fe – Fe separations in the structure.

Additional confirmatory evidence for a high-spin d^6 configuration on Fe is provided by the ^{57}Fe Mössbauer parameters $\delta = 1.10 \pm 0.05$ mm/s (relative to metallic iron) and $\frac{1}{2}eQV_{zz} = 2.62 \pm 0.05$ mm/s at 295 K. These values concur with those of Marfunin and Mkrtchyan[2]. The absence of a magnetic splitting in their spectrum at 80 K is also consistent with the failure to observe cooperative magnetism by the susceptibility method. The overall quadrupole splitting

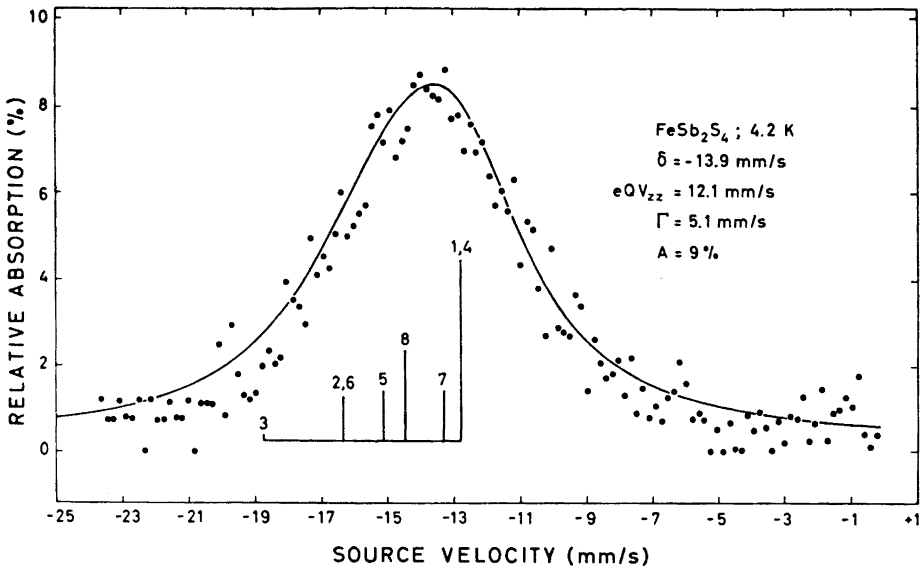

Fig. 1. ^{121}Sb Mössbauer spectrum of berthierite ($FeSb_2S_4$) at 4.2 K.

is, in this case, determined by the electronic imbalance in the essentially non-bonding and anti-bonding 3*d* orbitals on Fe and the asymmetric electron distribution of the Fe–S bonding orbitals consequent on the deviation from cubic symmetry of the Fe environment. The major contribution to the quadrupole splitting in high-spin Fe(II) compounds clearly arises from the former effect, although the influence of distortion is not insignificant at (say) room temperature. Ganiel [10] points out that the low temperature "saturation" value of the quadrupole splitting is independent on the site symmetry of the Fe atoms.

Fig. 1 shows the ^{121}Sb Mössbauer spectrum of $FeSb_2S_4$ taken at 4.2 K. Despite the presence of two distinct crystallographic Sb sites, their individual contributions could not be resolved and the parameters given on the diagram were obtained on the assumption of a single Sb site. Similar observations have been made for compounds with the $CoSb_2$ type structure and for Sb_2S_3.[5,11] For the latter compound, however, a significant line-broadening is reported as is also the case for $FeSb_2S_4$.

The ^{121}Sb chemical shift in $FeSb_2S_4$ is in the region typical for Sb(III) compounds.[14] (The shift for InSb is −9.0 mm/s at 4.2 K.) A non-bonding electron pair can only contribute to the overall quadrupole iteration when it possesses *p* (or *d*) character. The magnitude and positive sign of eQV_{zz} (*i.e.* negative V_{zz}) in this case, are thus consistent with a filled, non-bonding orbital with high *p* character localized on each Sb atom. The value of eQV_{zz} in $FeSb_2S_4$ is comparable with that obtained from nuclear quadrupole resonance experiments for Sb_2S_3.[12]

In general, in an inorganic macromolecule of the type considered here, an increase in the bond length between the metal and non-metal atoms (decreasing bond strength) is paralleled by a decrease in the non-metal to non-metal bond length (increasing bond strength). Such an effect has, for example, been observed in compounds with the pyrite, marcasite, and arsenopyrite type structures.[13] Thus, the long Fe–S bond lengths and the high-spin state of the Fe atoms observed in $FeSb_2S_4$ reflect the strong bonding within the SbS_3 groups. The average Sb–S bond length of 2.50 Å in $FeSb_2S_4$ is even shorter than that reported for amorphous Sb_2S_3 (2.60 Å) which in turn is considerably shorter than in crystalline Sb_2S_3 (2.80 Å).[15] The conclusion is accordingly that the bonding in $FeSb_2S_4$ is predominantly covalent as opposed to the ionic picture considered earlier.[2,3]

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