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Mössbauer effect study of ^{57}Fe and ^{119}Sn in stannite, stannoidite, and mawsonite

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Abstract

The valency formulae of minerals in the system Cu–Fe–Sn–S were determined with the aid of electron probe microanalysis and of the Mössbauer effect study of ^{57}Fe and ^{119}Sn at temperatures of 80°K and 293°K. The formulae of stannite, stannoidite, and mawsonite can be expressed as $Cu_2^{1+}(Fe^{2+}, Zn^{2+})\ Sn^{4+}S_4^{2-}$, $Cu_8^{1+}Fe_2^{3+}(Fe^{2+}, Zn^{2+})\ Sn_2^{4+}S_{12}^{2-}$, and $Cu_6^{1+}Fe_2^{3+}Sn^{4+}S_8^{2-}$ respectively. Zn was found to substitute only for the ferrous ion. Mawsonite contains no zinc.

The quadrupole splittings and isomer shifts could be rationalized with crystal field effects caused by the differences in site symmetry around the Fe and Sn atoms. Quadrupole splittings and isomer shifts of ^{119}Sn indicate that the (SnS_4)-tetrahedron of these specimens is strongly covanently bonded, and that it may be regarded as a chemical radical bearing sp^3 hybrid orbitals. Site symmetries around tin atoms in these structures are similar.

The most probable space group of mawsonite is $I\bar{4}2m$, $I4mm$, $I422$, or $I4_122$, based on its X-ray powder diffraction pattern and the site symmetries of tin and iron ions determined from the Mössbauer effect study.

Introduction

Mawsonite, stannoidite, stannite, and rhodostannite are minerals in the system Cu–Fe–Sn–S. Some of their crystal structures are said to be similar to that of chalcopyrite. Markham and Lawrence (1965) stated that mawsonite was pseudocubic, with the chemical formula $Cu_7Fe_2SnS_{10}$. Kato and Fujiki (1969) described stannoidite as orthorhombic with chemical composition $Cu_5Fe_2SnS_8$. Boorman and Abbott (1967), Springer (1968), and Petruk (1973) reexamined the chemical compositions of these specimens and defined stannoidite as $Cu_8(Zn,Fe)_3Sn_2S_{12}$ and mawsonite as $Cu_6Fe_2SnS_8$.

Springer (1972) showed in his work on phase equilibrium diagram for Cu_2FeSnS_4–Cu_2ZnSnS_4 that at a temperature above 680°C synthetic stannite forms a solid solution with synthetic kesterite in the whole range of zinc-iron substitution; that the former has polymorphic structures of α-phase and β-phase; and that the increased Zn substitution in stannite will reduce the temperature of transition between the two phases.

The crystal structure of stannite analyzed by Brockway (1934) is closely analogous to that of chalcopyrite. Further, the crystal structure of stannoidite has recently been analyzed by Kudoh and Takéuchi (1974). This structure indeed resembles that of chalcopyrite, but is more deformed compared to stannite because of the presence of additional interstitial cations. Stannoidite has four copper sites, two iron sites, and one tin site. The structures of other minerals in the above-mentioned system are still not defined.

The cation valences of these minerals are still ambiguous, because chemical analyses have not been conducted in consideration of the valency states of cations. Since iron, copper, and tin may all have several valencies in crystalline phases, complications arise in defining the valencies of these cations.

Pauling and Brockway (1932) and Hall and Stewart (1973) discussed the valency formula of chalcopyrite from the bond lengths determined by X-ray crystal analysis, and they reported that chalcopyrite is a mixture of two states $Cu^{1+}Fe^{3+}S_2^{2-}$ and $Cu^{2+}Fe^{2+}S_2^{2-}$. But the neutron diffraction study by Donnay *et al.*

(1958) and Mössbauer effect study by Chandra and Puri (1968) show that the iron ion in chalcopyrite has a single trivalent state.

The Mössbauer effect can determine the charge valencies of iron ions. The cation valence of Fe in stannite has been determined by several investigators Eibschutz *et al.* (1967), Marfunin and Mkrtchyan (1967), and Greenwood and Whitfield (1968).

The present study eliminates the ambiguity about the valency formulae of stannoidite and mawsonite as well as stannite with the aid of the Mössbauer spectra of both ^{57}Fe and ^{119}Sn. It also discusses the site symmetries of iron and tin and of the character of Fe–S and Sn–S bonds in these minerals in comparison with synthetic samples and some other sulfides such as chalcopyrite and sphalerite.

Material and experimental method

Stannite from Gyojayama, Kyoto Prefecture, and stannoidite and mawsonite from the Akenobe mine, Hyogo Prefecture, were separated from the ores under the ore microscope and by the subsequent crushing, magnetic, and specific gravity separations. The occurrence and paragenesis of these minerals were reported by Lee *et al.* (1974). Synthetic Cu_2FeSnS_4 and $Cu_8Fe_3Sn_2S_{12}$ were prepared in an evacuated silica tube and identified by the ore microscopic and X-ray powder diffraction methods. Their homogeneities were confirmed by electron microprobe. Chalcopyrite from the Arakawa mine, Akita Prefecture, and cubanite from the Kohmori mine, Kyoto Prefecture, were employed for reference. Some of the natural samples were analyzed by the electron microprobe method, using a computer program modified on the basis of the correction formula devised by Sweetman and Long (1969), as shown in Table 1. Their recalculations gave an empirical formula for each specimen. These were in good agreement with the previously reported formula of stannite (Ramdohr, 1960; Oen, 1970), stannoidite (Petruk, 1973) and mawsonite (Petruk, 1973; Kulichikhina and Vyal'sov, 1969).

TABLE 1. Chemical analysis of specimens in the system Cu–Fe–Sn–S

	Stannite		Stannoidite		Mawsonite	
	wt%	mol%	wt%	mol%	wt%	mol%
Cu	30.11	24.77	38.49	31.69	44.15	35.48
Fe	13.44	12.58	10.04	9.41	12.95	11.84
Zn	1.07	0.86	3.62	2.90	0.00	0.00
Sn	28.55	12.59	18.89	8.33	14.58	6.27
S	30.18	49.21	29.21	47.67	29.14	46.41
Total	103.35	100.00	100.26	100.00	100.82	100.00
Empirical Formula	$Cu_2(Fe,Zn)SnS_4$		$Cu_8(Fe,Zn)_3Sn_2S_{12}$		$Cu_6Fe_2SnS_8$	

TABLE 2. Cell dimension of specimens

Stannite	Stannoidite	Mawsonite
a = 5.461 + 0.002	a = 10.789 + 0.009	a = 10.745 + 0.001
	b = 5.413 + 0.004	
c = 10.726 + 0.007	c = 16.155 + 0.009	c = 10.711 + 0.006
S.G. $I\bar{4}2m$ (1)	S.G. I222 (2)	Presumable S.G. I42m, I4mm (3) I422, $I4_122$

(1) Brockway (1934)

(2) Kudoh and Takeuchi (1974)

(3) Present assumption

Cell dimensions of stannite, stannoidite, and mawsonite were obtained by X-ray powder diffractometry and were calculated with the aid of least-squares method using UNICS computer program. The cell dimensions of the samples are presented in Table 2. Mawsonite was reported to be pseudocubic by Markham and Lawrence (1965), Levy (1967), and Kulichikhina and Vyal'sov (1969). Better indexing of the mawsonite pattern using the computer program written by Evans *et al.* (1963) implied tetragonal symmetry as shown in Table 3.

Mössbauer spectra of ^{57}Fe and ^{119}Sn in the natural and synthetic materials were obtained at 80°K and at room temperature (293°K) by using a HITACHI/RAH/-403, 400 channel analyser. ^{57}Co diffused in metallic copper (10 millicuries) and ^{119m}Sn doped in $BaSnO_3$ (2 millicuries) were used as sources. These γ-ray sources have fairly large recoilless fractions and give absorption peaks with very narrow-line widths. The line widths of the inner two lines of the spectrum of ^{57}Fe in metallic iron and those of the spectrum of ^{119}Sn in SnO_2 measured at room temperature were 0.30 mm/sec and 0.83 mm/sec, respectively, with these sources.

Spectra were taken by the mechanism of moving the source at both temperatures. Measurement at 80°K was conducted with both source and absorber in a cryostat.

The intensity of the 14.4 keV γ-ray emitted from ^{57}Co and the 23.8 keV γ-ray from ^{119m}Sn were detected by a NaI scintillation counter. The spectra of ^{57}Fe obtained at constant Doppler velocity calibrated by those in metallic iron were analyzed with the aid of a computer program which performed least mean squares fits of the experimental data to the Lorentzian function. This calculation did not employ a

TABLE 3. X-ray powder pattern of mawsonites from Mt. Lyell, Tasmania, and the Akenobe Mine, Hyogo Prefecture, Japan

1.		2.			
d(Å)	I	d_{obs}(Å)	d_{calc}(Å)	I_{obs}	h k l
		7.62	7.60	3	1 1 0
5.37	20	5.38	5.37	10	2 0 0
4.37	20	4.38	4.38	15	1 1 2
3.80	10	3.80	3.80	8	2 2 0
3.34	10	3.378	3.388	4	1 0 3
3.09	100	3.099	3.099	100	2 2 2
2.875	20	2.868	2.869	10	3 1 2
2.680	50	2.684	2.686	25	4 0 0
		2.462	2.461	3	1 1 4
2.395	10	2.401	2.401	8	4 0 2
2.287	10	2.291	2.289	5	3 3 2
2.185	5	2.192	2.192	3	4 2 2
2.098	5				
1.959	5	1.962	1.962	3	5 2 1
1.895	80	1.899	1.900	75	4 4 0
1.788	5	1.791	1.790	3	4 4 2
1.739	5	1.742	1.742	3	5 2 3
1.618	80	1.620	1.620	40	6 2 2
1.547	10	1.549	1.549	7	4 4 4
1.460	5	1.463	1.462	3	7 2 1
		1.366	1.365	3	6 5 1
1.343	20	1.344	1.343	15	8 0 0
		1.318	1.319	3	1 1 8
		1.302	1.302	4	6 4 4
1.232	30	1.233	1.232	10	6 6 2
1.201	5	1.201	1.201	5b	8 0 4
		1.096	1.096	15	8 4 4
a = 10.74 Å		a = 10.745 ± 0.0013			
c = 10.74 Å		c = 10.711 ± 0.0063			

1. *Mawsonite. Mt.Lyell, Tasmania. After Markham and Lawrence (1965). Co radiation. Camera method.*

2. *Mawsonite. Akenobe mine, Hyogo prefecture, Japan. Cu/Ni radiation. Diffractometer method. (b = broad).*

Gaussian component causing a deviation of line profile from the Lorentzian curve, although the true line shape may be closely approximated by a combination of Gaussian and Lorentzian functions.

The minimized variables were (1) peak position, (2) full width at half-maximum intensity, (3) peak intensity, and (4) off-resonance background count. Various numbers of peaks assumed to be present were tested for the best fit.

In the analysis of the ^{119}Sn spectra, a Pd-filter (70 μ thick) having a K-absorption edge of 24.3 keV was applied to eliminate the K-X-rays with energies of 25.04, 25.27 and 28.49 keV.

Isomer shifts of ^{57}Fe and ^{119}Sn spectra of each sample were measured with reference to the isomer shift of 310 stainless steel and SnO_2, respectively.

Experimental results and discussion

It has been proved that the isomer shift increases with decreases in s-electron density and increases in d-electron density in iron ion. The orbits of p- and d-electrons play the role of screening the s-electron from the positive electric charge of the nuclei. Fe^{2+} ($3d^6$), which has one more $3d$-electron than Fe^{3+} ($3d^5$), shows a larger screening effect and a decreased electron density around the iron nuclei, which causes the larger isomer shift for Fe^{2+}, (Walker *et al.*, 1962; Simanek *et al.*, 1968; Watson, 1960a, 1960b).

Covalency of Fe-anion bonds also influences the isomer shift. Increase in the ionic character of the bonds causes a decrease in the density of s-electrons around iron nuclei and raises the isomer shift in both ferric and ferrous ions.

The quadrupole splitting of ^{57}Fe depends on the electric field gradient at the iron nuclei, which is induced from the valency electrons and from the surrounding anions. The electric field gradient is also attributed to distortion of electron orbits due to the crystal field and the covalent bonding character, (Ingalls, 1962, 1964; Sternheimer, 1963). The electron cloud of Fe^{2+} is more likely to be distorted and more sensitive to the configuration of surrounding anions than that of Fe^{3+} and consequently expected to give a larger value of quadrupole splitting, while Fe^{3+} presents a spherically symmetric electron cloud. It must, however, be noted that in the case where the Fe^{2+} site symmetry is as high as cubic, Fe^{2+} compounds would show no or very small quadrupole splitting. The influence on the quadrupole splitting of the deviation of the symmetry of ligands from the cubic symmetry ($\bar{4}3m$) in sphalerite structure to the monoclinic (2) in stannoidite could be recognized in this study as shown in Table 4.

^{119}*Sn Mössbauer spectra*

Neutral tin has the electron configuration [Kr]($4d^{10}$)($5s^2$)($5p^2$). Sn^{4+} has the electron configuration [Kr]($4d^{10}$); Sn^{2+} has [Kr]($4d^{10}$)($5s^2$). Since tetravalent tin is little affected by contributions of the ($5s$) electron, the isomer shift of Sn^{4+} in ^{119}Sn Mössbauer spectra is very small. On the other hand, divalent tin ion exhibits a very pronounced isomer shift due to a large contribution of the ($5s^2$) electrons.

Increase of covalent character of Sn^{2+} results in the formation of ($5s^2$)($5p^x$) or other s-p hybrids thereby slightly reducing the isomer shift. Many covalent-bonded tin compounds consist of tetrahedral four-fold structures bearing (sp^3) hybrid orbitals, as do carbon compounds. In some cases, the ($5d$) orbital takes part resulting in the formation of trigonal dipyramidal five-fold coordination as the (sp^3d) hybrid

TABLE 4. Mössbauer spectra of ^{57}Fe at 293°K and 80°K

Specimen		293°K I.S. (mm/sec)	293°K Q.S. (mm/sec)	80°K I.S. (mm/sec)	80°K Q.S. (mm/sec)	Valency	Site symmetry
Mawsonite		0.53 ± 0.03	0.17 ± 0.03	0.56 ± 0.03	0.28 ± 0.03	Fe^{3+}	Unknown
Stannoidite	(I)	0.53 ± 0.03	0.34 ± 0.03	0.56 ± 0.03	0.39 ± 0.03	Fe^{3+}	2
	(II)	0.76 ± 0.06	2.86 ± 0.06	0.87 ± 0.08	3.08 ± 0.08	Fe^{2+}	222
Synthetic Stannoidite	(I)	0.50 ± 0.03	0.36 ± 0.03			Fe^{3+}	2
	(II)	0.76 ± 0.08	2.86 ± 0.08			Fe^{2+}	222
Stannite		0.78 ± 0.03	2.80 + 0.03	0.84 + 0.03	3.02 + 0.03	Fe^{2+}	$\bar{4}2m$
Synthetic Stannite		0.76 + 0.03	2.86 + 0.03			Fe^{2+}	$\bar{4}2m$
Chalcopyrite		0.34 + 0.03	0.00 + 0.00	0.50 + 0.03	0.00 + 0.03	Fe^{3+}	$\bar{4}$
Cubanite		0.50 + 0.03	0.88 + 0.03	0.53 + 0.03	1.01 + 0.03	Fe^{2+}	222
Sphalerite	^{57}Fe in (Zn,Fe)S	0.67 + 0.06	0.81 + 0.06	0.89 + 0.06	2.02 + 0.06	Fe^{2+}	$\bar{4}3m$

Doppler velocity is calibrated by the spectrum of ^{57}Fe *in metallic ion.*
Isomer shift (I.S.) *and quadrupole splitting* (Q.S.) *are relative to* ^{57}Fe *in 310 stainless steel.*

orbit or an octahedral six-fold coordination as the (sp^3d^2) hybrid. Within the same structural configuration, the isomer shift of compounds containing [SnX_4] and [SnX_6] groups decreases with the electronegativity of the surrounding anions (Stöckler and Sano, 1968).

The isomer shifts of ^{119}Sn in stannite, stannoidite, and mawsonite range from 1.45 ± 0.03 to 1.48 ± 0.03 mm/sec (Table 5). These values support the assumption that the SnS_4-tetrahedron of these minerals is strongly covalent and may be regarded as a chemical radical such as are found in sulphosalts.

The quadrupole splitting of ^{119}Sn is not an effective means for determining the electric charge of the tin ion. It has been proved that Mössbauer spectra of ionic Sn^{2+} compounds have a tendency to show a greater quadrupole splitting than those of Sn^{4+} compounds. This is because the latter compounds generally consist of highly symmetric coordinations around the tin ions. Furthermore, the higher the covalency of the Sn–X bonds, the less the interaction between the quadrupole splitting and electric charge of tin ion.

A seemingly single broad peak was observed in the ^{119}Sn spectra of stannite, stannoidite, and mawsonite. Little or no quadrupole splitting was detected even after computer processing the data. Some quadrupole splitting may be assumed to be present at least in the spectra of stannoidite from the fact that the site symmetry around the four-fold coordinated tin atom is (222), which deviates considerably from ($\bar{4}2m$) of stannite. The absence of observable quadrupole splitting probably results because the [SnS_4] group does not have a sufficiently large electric field gradient around the tin ion. The minerals are each confirmed to have only one strongly covalently bonded four-fold coordinated Sn^{4+} ion. The fact that the isomer shift and quadrupole splitting of ^{119}Sn is nearly identical in all three minerals suggests that the tin coordination is very similar although the site symmetry of the ion may be different.

In spite of the anomalously long Fe–S bond lengths in the system (for example, 2.36 Å in stannite) and the high site symmetry, ^{57}Fe Mössbauer spectra of stannite and stannoidite show a much larger quadrupole splitting than that of other sulfides containing iron atoms. This may be explained by the fact that an iron atom bridges two (SnS_4) tetrahedra which are strongly covalently bonded groups, and that the Fe–S bonds may also have largely covalent character.

^{57}Fe Mössbauer spectra

Stannite. The isomer-shifts of natural and synthetic stannite prove the iron to be divalent ($3d^6$). The small values compared with isomer shifts in many other ferrous compounds confirm the existence of

TABLE 5. Mössbauer spectra of ^{119}Sn

Specimen	I.S. (mm/sec)	Q.S. (mm/sec)	Valency	Site symmetry
Mawsonite	1.46 + 0.05	0.00 + 0.05	$(SnS_4)^{2-}$	unknown
Stannoidite	1.48 + 0.05	0.00 + 0.05	$(SnS_4)^{2-}$	2
Stannite	1.45 + 0.05	0.00 + 0.05	$(SnS_4)^{2-}$	$\bar{4}2m$
Synthetic SnS	3.48 + 0.03	0.91 + 0.05	Sn^{2-}	m
Cassiterite SnO_2	0.00 + 0.03	0.40 + 0.05	Sn^{4+}	mmm

Isomer shift (I.S.) *and quadrupole splitting* (Q.S.) *are relative to* ^{119}Sn *in the synthetic* SnO_2

highly covalent bonds. In spite of the $\bar{4}2m$ symmetry of iron ions in stannite, the exceedingly large quadrupole splitting also indicates the presence of the covalent bonds. This may be because iron shares one of sulfur ions of $(SnS_4)^{4-}$ group having the aforementioned (sp^3) hybrid bonds.

Synthetic stannite having no zinc content shows a higher absorption peak, a slightly smaller isomer-shift and a little larger quadrupole splitting than those parameters for natural stannite having 9 mole percent of zinc. It may be concluded that zinc substitutes for ferrous ion and increases the ionicity of its bonding.

Stannoidite. There exist two pairs of doublets in the Mössbauer spectra of natural and synthetic stannoidite. Isomer shift and quadrupole splitting of the inner and outer doublets prove the existence of both ferrous and ferric ions in stannoidite. The observed absorption intensity (2.38%) of the inner doublet of zinc-free synthetic stannoidite is almost twice as much as that of the outer one (1.21%). Since it can be reliably assumed that each recoilless fraction and saturation effect is not very different at the two iron sites of stannoidite because of the same effective width of the absorber and identical site symmetries, the ratio of absorption intensities of the inner and outer doublets may be regarded as the fraction of ferric and ferrous ions in these sites. Accordingly, the zinc-free stannoidite is proved to contain twice as much ferric ion as ferrous ion and can be expressed as $Cu_8^{1+}Fe_2^{3+}Fe^{2+}Sn_2^{4+}S_{12}^{2-}$.

The outer doublet corresponding to the ferrous ion of the synthetic stannoidite has a larger absorption peak than that of the natural material containing 2.90 mole percent of zinc ion, while the absorption intensities of the inner doublet has about the same intensity in both specimens. This suggests that zinc substitutes only on ferrous sites in stannoidite. The above values indicate 70.6 percent of zinc substitution in the ferrous ion site. Zinc substitution can probably reach the ratio of Zn/(Zn + Fe) = ⅓ at most.

Mawsonite. The present analysis shows mawsonite to have the formula $Cu_6Fe_2SnS_8$ as previously reported by Petruk (1973). No substitution of zinc for iron in mawsonite is observed. Mawsonite is unable to admit a divalent cation such as zinc, probably because mawsonite contains only ferric iron.

The Mössbauer effect study gives the valency formula of mawsonite as $Cu_6^{1+}Fe_2^{3+}Sn^{4+}S_8^{2-}$. The quadrupole splitting and isomer shift of ^{119}Sn are very similar to those of stannite and stannoidite. Only one ^{57}Fe doublet is observed, and its quadrupole splitting and isomer shift are about the same as those of the inner doublet (I) in the spectra of stannoidite, indicating the existence of ferric ion in an analogous coordination.

Though the crystal structure of mawsonite has not been analyzed because of difficulties in obtaining a single crystal, the present X-ray powder diffraction data and the Mössbauer spectrum have considerably clarified the structure. The most probable space group is $I\bar{4}2m$, $I4mm$, $I422$ or $I4_122$ to be consistent with site symmetries around the tin and iron ions determined from the Mössbauer effect study as well as of the indices of powder diffraction peaks.

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