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# CHALCOGENIDES OF THE TRANSITION ELEMENTS. VII. A MÖSSBAUER STUDY OF PENTLANDITE[1]

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## ABSTRACT

Mössbauer spectra of $Fe^{57}$ were obtained from natural and annealed Sudbury pentlandite at temperatures between ambient and 4.2°K. Their analysis leads to the conclusion that the irreversible expansion of the unit cell which takes place on annealing at 200°C in vacuo is caused by migration of Fe atoms from the octahedrally coordinated 4(*b*) sites of *Fm*3*m* to the tetrahedrally coordinated 32(*f*) sites. The initial population of the 4(*b*) sites by Fe atoms is larger, and the final population smaller, than would correspond to a completely random distribution of the metal atoms over the 4(*b*)+32(*f*) sites. There is no evidence of magnetic ordering in pentlandite even at 4.2°K. The Mössbauer parameters of the Fe atom at 4(*b*) are consistent with divalent iron involved in appreciable covalent bonding. The ground state of the Fe atom at 32(*f*) cannot be ascertained from the present Mössbauer evidence alone.

The lattice parameter of natural pentlandite, $(Fe, Ni)_9S_8$, is smaller than that of synthetic pentlandite of the same composition (Knop *et al.*, 1965). However, on heating to temperatures between 150 and 200°C under nonoxidizing conditions (vacuum or argon) the structure of natural pentlandite undergoes an irreversible expansion, whereby *a* increases by about $\frac{1}{2}$ percent and is brought into the *a* range of the synthetic pentlandite. Exposing the sulfide to temperatures in excess of 200°C did not seem to produce additional increase in *a*. The expansion took place even when the mineral was heated under 2000 atm of argon.

In natural pentlandite the atomic ratio Ni:Fe is usually between 1 and 1.15 (Knop *et al.*, 1965). In synthetic pentlandite it can be varied between approximately 3:1 and 1:3; the lattice parameter of the cubic pentlandite ($\pi$) phase increases nonlinearly with increasing Fe content (Knop and Ibrahim, 1961). The 36 metal atoms in the unit cell of the $\pi$ structure are distributed, ideally, over the 4(*b*) and 32(*f*) sites of *Fm*3*m*. A complete ordering with respect to these two equipoints would only be possible if the Ni:Fe ratio were 8:1 or 1:8. These values are far from the Ni:Fe ratios commonly observed in the mineral, and in fact far outside the limits of the stability range of synthetic $\pi$(Fe, Ni, S). Regardless of whether 4(*b*) is occupied by 4 Fe or 4 Ni or 4 (Fe, Ni), 32(*f*) must

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[1] For Part VI see Knop *et al.* (1968).

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thus always accommodate *both* Fe and Ni atoms, most likely in a statistical distribution. The actual number of Fe and Ni atoms in 32(*f*) will depend on the analytical Ni:Fe ratio of the $\pi$ phase and on the number of Fe atoms in 4(*b*). But, barring a drastic variation in the number of intrinsic vacancies with the Ni:Fe ratio, a steady increase in $a(\pi)$ on traversing the Ni:Fe composition range from 3:1 to 1:3 can only result if the effective size of the Fe atom in the structure is larger than that of the Ni atom. The Fe atoms responsible for the increase will therefore be located in the tetrahedrally coordinated 32(*f*) sites.

The composition of natural pentlandite does not appear to change on expansion: no foreign lines were observed in the X-ray powder photographs of the annealed material. The possibility thus exists that the irreversible expansion of the pentlandite structure is caused by a redistribution of the metal atoms between the 4(*b*) and 32(*f*) equipoints, in which Fe atoms migrate from 4(*b*) to 32(*f*). Alternatively, the annealed and the synthetic pentlandites may contain a greater fraction of vacant sites on each of the sublattices of the $\pi$ structure than the natural material, with essentially no change in the Ni:Fe ratios in 4(*b*) and 32(*f*) and in the mode of distribution of the metal atoms in these equipoints. The distribution of the Fe and Ni atoms is, however, not known, so any attempt to demonstrate a redistribution must start from a determination of the numbers of atoms of each kind in 4(*b*) and 32(*f*).

X-ray diffraction is ineffective because of the close similarity of the X-ray scattering factors of Fe and Ni, although anomalous-scattering experiments might yield some information. Neutron diffraction can be expected only marginally effective for a similar reason. The coherent scattering amplitudes of Fe and Ni for neutrons are, for natural isotopic contents, 0.96 and $1.03 \times 10^{-12}$ cm respectively, and thus too close to enable differences between mixed populations of the two equipoints to be determined with confidence. Mössbauer spectroscopy should, however, prove useful, at least on theoretical expectation, and it was the aim of the present investigation to use this method to elucidate the distribution of the metal atoms in the mineral.

## EXPERIMENTAL

The pentlandite used in this investigation was extracted from specimens of coarsely crystalline ore from Creighton Mine, Sudbury, Ont., by careful handpicking, crushing and magnetic separation. It was the same material as *S* of Knop *et al.* (1965). On annealing the natural material (100 mesh; $a = 10.044 \pm 0.001$ Å) for 53 hr at 200°C in vacuo and cooling with the oven, the lattice parameter increased to $10.105 \pm 0.001$ Å, in excellent agreement with results reported in our previous work.

Densities were determined by weighing in air and in $CCl_4$. To minimize the effect of trapped air the fine powder, in a thin-walled aluminum thimble, was placed in a special glass apparatus (Barker, 1966) whose side-arm contained $CCl_4$ frozen with liquid nitrogen. The apparatus was carefully evacuated, isolated from the vacuum line by closing the connecting stopcock, and the $CCl_4$ was thawed and distilled onto the powder. The density of selected small quartz crystals (Herkimer diamonds), which were used to check the method, was determined as $2.657 \pm 0.003$ g/cm³.

The observed densities of the natural and the annealed pentlandite at 22–24°C (means of 4 determinations each) were $5.060 \pm 0.009$ and $4.958 \pm 0.007$ g/cm³ respectively. This is in good agreement with the values of $5.067 \pm 0.002$ and $4.974 \pm 0.002$ g/cm³ calculated from the measured $a$ taking $Z=4$ and $N=6.0226 \times 10^{23}$.

Mössbauer spectra of the pentlandites were recorded on spectrometers at the University of East Anglia, Norwich, and the University of Exeter. The instruments were both of the conventional constant-acceleration electromechanical type, based on 400-channel multichannel analyzers operating in the multiscaler mode. The drive system was based on a design due to Clark *et al.* (1967). The $\gamma$-ray detector was a 0.015-in. NaI(Tl) scintillator mounted on a 1-in. photomultiplier. The sources used were $Co^{57}$ in Pd at room temperatures and had original intensities of about 10 mCi. Calibration of the spectrometers was carried out using a thin iron foil and applying the data of Preston *et al.* (1962). Isomer shifts are quoted relative to metallic iron. To convert to stainless steel add +0.090 mm/s and to sodium nitroprusside dihydrate, +0.257 mm/s (Muir *et al.*, 1967).

Absorbers for room-temperature spectra were prepared by dispersing pentlandite powder in acrylic disks machined down to about 1 mm thickness. Each disk contained about 3 mg/cm² of natural iron, so no appreciable thickness effects would be expected from such essentially "thin" absorbers. For low-temperature spectra absorbers were made by mounting a thin layer of powder onto an iron-free Al backing foil with durafix cement. The variable-temperature cryostat was capable of operating between 4.2°K and room temperature. The absorber temperature was measured with a 0.03 at. percent Fe in Au *vs.* chromel thermocouple and stabilized by a simple thermostat system (Woodhams *et al.*, 1966).

The Mössbauer spectra were fitted to a number of overlapping Lorentzian-shaped lines by a standard iterative least-squares technique. The program minimized $\chi^2$, the sum of the squared deviations from the assumed function divided by the variance at a single channel, and gave the most probable estimates of the line parameters together with their standard deviations.

## RESULTS AND DISCUSSION

*Densities.* The agreement of the observed densities with the densities calculated for full occupancy of the pentlandite unit cell indicates that the intrinsic defectiveness of the structure, *i.e.* equal percentage of vacancies in 32(*f*), 4(*b*), 24(*e*), and 8(*c*), is quite small: the difference between the calculated and the observed densities was only ($0.14 \pm 0.22$) percent for the natural and ($0.32 \pm 0.18$) percent for the annealed material. In view of the uncertainties involved the difference cannot be confidently claimed to have increased on annealing. Change in the degree of defectiveness of the structure can thus be at most a contributory factor in the irreversible volume increase on heating.

*The Mössbauer Spectrum.* Typical spectra of natural and annealed pent-

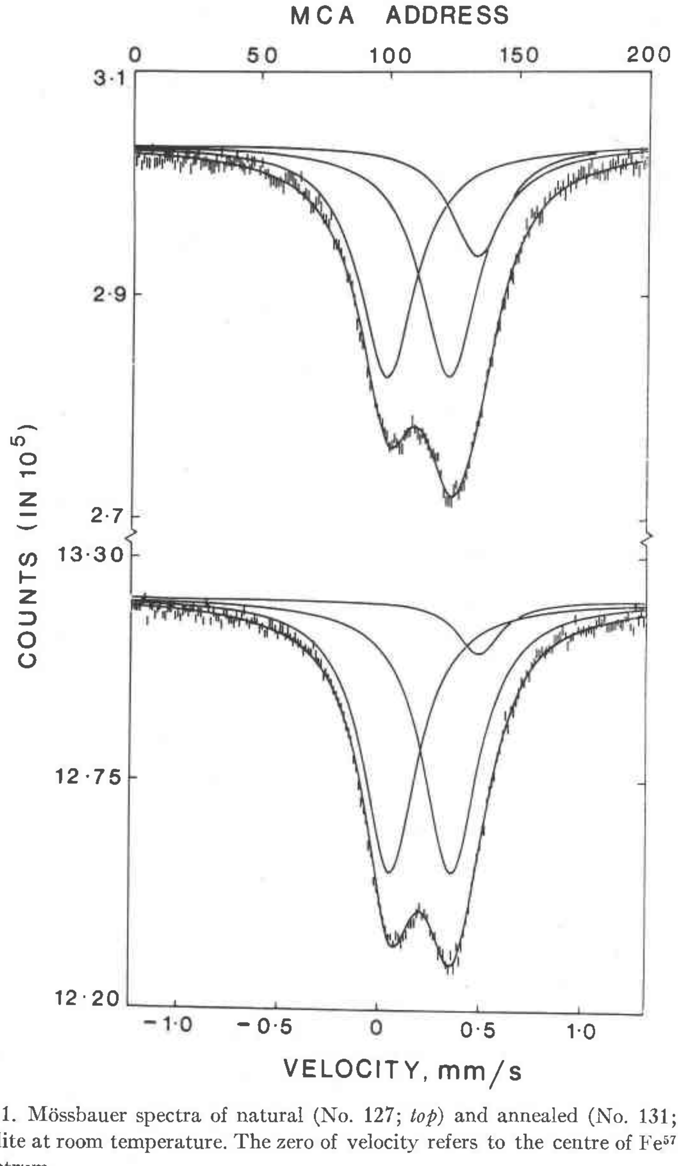

FIG. 1. Mössbauer spectra of natural (No. 127; *top*) and annealed (No. 131; *bottom*) pentlandite at room temperature. The zero of velocity refers to the centre of $Fe^{57}$ calibration spectrum.

landite at room temperature are shown in Figure 1.[1] The spectra appear to consist of an asymmetric doublet, the asymmetry being larger in the

[1] The spectrum of natural pentlandite from Noril'sk (composition not stated) reproduced in Marfunin and Mkrtchyan's paper (1967) seems to be presented as a symmetric quadrupole doublet.

natural than in the annealed material. All the spectra were similar and reproducible, regardless of the spectrometer used, and there was no significant change on cooling the specimens. In particular, no evidence of magnetic ordering was observed even at 4.2°K.

Asymmetry in a quadrupole doublet may arise from one or more of the following: (i) preferential orientation of the crystal particles in the absorber; (ii) anisotropy of the recoil-free fraction for atoms in sites of lower than cubic symmetry (the Gol'danskii-Karyagin effect); (iii) paramagnetic relaxation effects; and (iv) a complex spectrum arising from superposed spectra of Fe atoms in different types of sites. The temperature independence of the observed asymmetry rules out the Gol'danskii-Karyagin and relaxation possibilities, while (i) is discounted by the cubic symmetry of the sample: experiments with powder of smaller particle size, and varying the angle between the absorber and the source-detector axis, produced no change in the spectra. Thus we believe the asymmetry is due to (iv).

The Creighton Mine pentlandite used in this investigation analyzed to $Fe_{4.20}Co_{0.06}Ni_{4.74}S_8$, *i.e.* $(Ni+Co):Fe=1.14$, with $17\pm1$ Fe atoms per unit cell (Knop *et al.*, 1965). Since the 4(*b*) sites can accommodate at most 4 Fe atoms the majority of the Fe atoms must be located in the tetrahedrally coordinated 32(*f*) sites. The spectrum will thus be dominated by absorption by $Fe^{57}$ nuclei in these sites. The $FeS_4$ tetrahedra exhibit trigonal ($3m$) distortion and a quadrupole doublet is expected. However, when $x=1/8$, and when at the same time the positional parameter $u$ of the S atom in 24(*e*) is $\frac{1}{4}$, the tetrahedra become metrically regular.[1] In these circumstances the contribution of the ligand environment to the electric field gradient at the Fe nucleus in $FeS_4$ might conceivably be very small. In the simultaneous absence of an electric field gradient from non-symmetric orbital occupancy by uncompensated electrons the ex-

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[1] The actual symmetry at any $Fe_f$ atom is, strictly speaking, always lower than $3m$, although on Bragg diffraction criteria the site symmetry required by the space group is satisfied by volume-averaging for the crystal as a whole, quite apart from the close similarity of the atomic scattering factors of Fe and Ni. In $Fe_{4.5}Ni_{4.5}S_8$ with Fe and Ni distributed at random the fraction of $FeS_4$ tetrahedra surrounded by *only* Fe or *only* Ni atoms as nearest metal-atom neighbours is 25 percent (Barker and Knop, 1970). When the symmetry of the $FeS_4$ aggregates including progressively more distant metal-atom neighbours is considered, the fraction of $Fe_f$ atoms that have extensive environments of symmetry $3m$ tends to zero. Even assuming that only nearest metal-atom neighbours affect the electric field gradient at the Fe atom in an $FeS_4$ tetrahedon significantly, the observed quadrupole splitting (and probably also the isomer shift) will be the result of a superposition of several values, each corresponding to one type of environment; the frequency distribution of the possible types of environment in the crystal will depend on the Ni:Fe ratio and on the degree of order in 4(*b*). However, the observed smallness of the quadrupole splitting and line widths (see later in the text) seems to indicate that atoms beyond the nearest S neighbours have little effect on the features of the Mössbauer spectrum.

pected quadrupole doublet would not be resolved and would appear as a broadened single line.

The site symmetry of atoms in the octahedrally coordinated 4(*b*) sites is cubic (*m*3*m*).[1] When 4(*b*) contains only Ni atoms, the resulting spectrum is just that from the 17 $Fe_f$ atoms. However, when 4(*b*) is completely or partially occupied by Fe atoms, a single line, or a quadrupole doublet, of lower intensity will appear.[2] For not too large a difference in the isomer shifts at $Fe_f$ and $Fe_b$ the resulting spectrum would consist of an asymmetric single line or an asymmetric doublet. The ratio *R* of the areas under the component spectra will be equal to the ratio of the number of Fe atoms in 32(*f*) and 4(*b*), Fe(*f*) : Fe(*b*), if the recoil-free fractions at the two sites are equal and relaxation effects are absent. This assumption is reasonable in this case as *R* does not vary with temperature (see below).

As asymmetric doublet of the type shown in Figure 1 can be considered then as arising from (a) two independent single lines, or (b) a single line superposed on a symmetric quadrupole doublet, or (c) a weak doublet superposed on a dominant symmetric quadrupole doublet. When spectra 127 and 131 were fitted to cases (a) and (b) $\chi^2$ tests of the goodness of fit showed that $\chi^2$(b) was significantly lower, by about 40 in 250, than $\chi^2$ (a). This was taken as good evidence that (b) is the more acceptable model. Spectrum 127 was also fitted to case (c). This fit gave a similar $\chi^2$ as for fit (b), so that either model is statistically acceptable. The quadrupole splitting at $Fe_b$ is only about 0.1 mm/s, *i.e.* less than one-half of a line width, and the isomer shift is the same as for fit (b). In view of this we decided to fit all the pentlandite spectra to model (b) but the fitted single line may possibly be a temperature-independent unresolved doublet. No constraints were placed on the line parameters for case (a), but for (b) and (c) the widths and intensities of the doublet lines were constrained to be equal.

In addition to the statistical evidence the following physical facts should be considered. As pointed out above, spectra of the same type were obtained under a variety of conditions. For case (a), the two inde-

[1] Similar arguments as described in the preceding footnote apply *a fortiori* to the $FeS_6$ octahedra at 4(*b*). For a pentlandite with Ni : Fe = 1 the fraction of $FeS_6$ octahedra having an *m*3*m* symmetry with respect to their nearest metal-atom neighbours, is in fact completely negligible (Barker and Knop, 1970).

[2] Whether the spectrum from $Fe_b$ is a single line or a quadrupole doublet will depend on the electronic configuration of the atom. The *a priori* probable configurations are $3d^6$ or $3d^5$. The occupancy of the 3*d* orbitals is of cubic symmetry for low-spin $3d^6$ and high-spin $3d^5$, so there can be no quadrupole splitting from this source. In a cubic ligand field the splitting would be zero even for the high-spin $3d^6$ and low-spin $3d^5$ configurations, unless the degeneracy of the $d_\epsilon$ level were removed by some perturbing influence (*e.g.* the noncooperative Jahn-Teller effect, spin-orbit coupling) (*cf.* Ingalls, 1962).

TABLE 1. MÖSSBAUER $Fe^{57}$ PARAMETERS OF CREIGHTON MINE PENTLANDITE[a]

| Sample | Run No. | Temperature, °K | Quadrupole spectrum *QS* | Quadrupole spectrum *IS* | Quadrupole spectrum *LW* | Single-line spectrum *IS* | Single-line spectrum *LW* | Area ratio, *R* |
|---|---|---|---|---|---|---|---|---|
| | | | <100 mesh (Norwich spectrometer) | | | | | |
| Natural | 125 | R.T. | 0.298(5) | 0.356(8) | 0.298(8) | 0.649(8) | 0.28(2) | 4.4±0.5 |
| Annealed | 123 | R.T. | 0.29(1) | 0.37(1) | 0.311(8) | 0.65(2) | 0.23(5) | 15.5±5.0 |
| | | | <100 mesh (Exeter spectrometer) | | | | | |
| Natural | 127 | R.T. | 0.312(5) | 0.361(5) | 0.347(5) | 0.657(4) | 0.32(1) | 4.5±0.5 |
| | 128 | 97 | 0.364(6) | 0.457(5) | 0.372(6) | 0.787(5) | 0.27(1) | 6.6±0.3 |
| | 129 | 33 | 0.371(5) | 0.466(4) | 0.371(6) | 0.803(4) | 0.31(1) | 5.4±0.3 |
| | 130 | 4.2 | 0.358(8) | 0.461(5) | 0.411(8) | 0.809(5) | 0.34(2) | 4.5±0.3 |
| Annealed | 131 | R.T. | 0.304(2) | 0.385(2) | 0.336(3) | 0.675(4) | 0.265(8) | 13±1 |
| | | | <250 mesh (Exeter spectrometer) | | | | | |
| Natural | 139 | 77 | 0.351(16) | 0.452(10) | 0.386(16) | 0.779(10) | 0.29(2) | 5.7±1.2 |
| | 140 | 4.2 | 0.338(18) | 0.445(18) | 0.398(16) | 0.779(8) | 0.31(2) | 4.7±1.0 |
| Annealed | 138 | R.T. | 0.310(7) | 0.383(6) | 0.390(4) | 0.686(7) | 0.27(2) | 15±2 |
| | 148 | R.T. | 0.294(16) | 0.380(16) | 0.352(10) | 0.66(2) | 0.32(8) | 15±3 |
| | 149 | 77 | 0.354(14) | 0.477(16) | 0.380(12) | 0.866(16) | 0.22(6) | 19±8 |
| | 144 | 4.2 | 0.354(16) | 0.475(18) | 0.397(14) | 0.790(14) | 0.21(2) | 16±6 |

[a] *QS*, quadrupole splitting; *IS*, isomer shift relative to metallic iron; *LW*, line width. All values in mm/s. The standard deviations are in units of the last decimal of the parameter values: 0.338(18) stands for 0.338 ±0.018 etc. For *R* the standard deviations are quoted in full.

pendent single lines could arise if the $FeS_4$ tetrahedra in 32(*f*) were regular or nearly so, or if a large degree of covalency were present (cf. Okiji and Kanamori, 1964; Ôno *et al.*, 1962), and these possibilities must be considered. However, the smallest possible value *R* can assume is 13:4=3.25, *i.e.* almost 3:1. If the doublets of Figure 1 are taken to consist of two single lines, inspection shows that ratio of the areas would be less than 3:1. But this cannot be reconciled with the structure of pentlandite.

Model (b) fits the observed spectra into components illustrated in Figure 1. The quadrupole splittings and isomer shifts of these components for the individual experiments are listed in Table 1. It is immediately seen that the ratios of the areas doublet:singlet are all larger than 3.25, as required. The parameters of Table 1 are compared with the reported isomer shifts and quadrupole splittings for pyrite and marcasite-type compounds in Figure 2.

The line widths are broadened slightly compared to the value of 0.23 mm/s obtained with a natural iron absorber. The broadening for the 32(*f*) sites increases with decreasing temperature.

*Effect of annealing.* *R* varies with Fe(*b*) as [(17±1)−Fe(*b*)]/Fe(*b*) (Fig. 3). The weighted mean $\overline{R}=\overline{A}$(quadrupole doublet):$\overline{A}$(single line) for the pairs 125–123 (room temperature), 127–131 (room temperature),

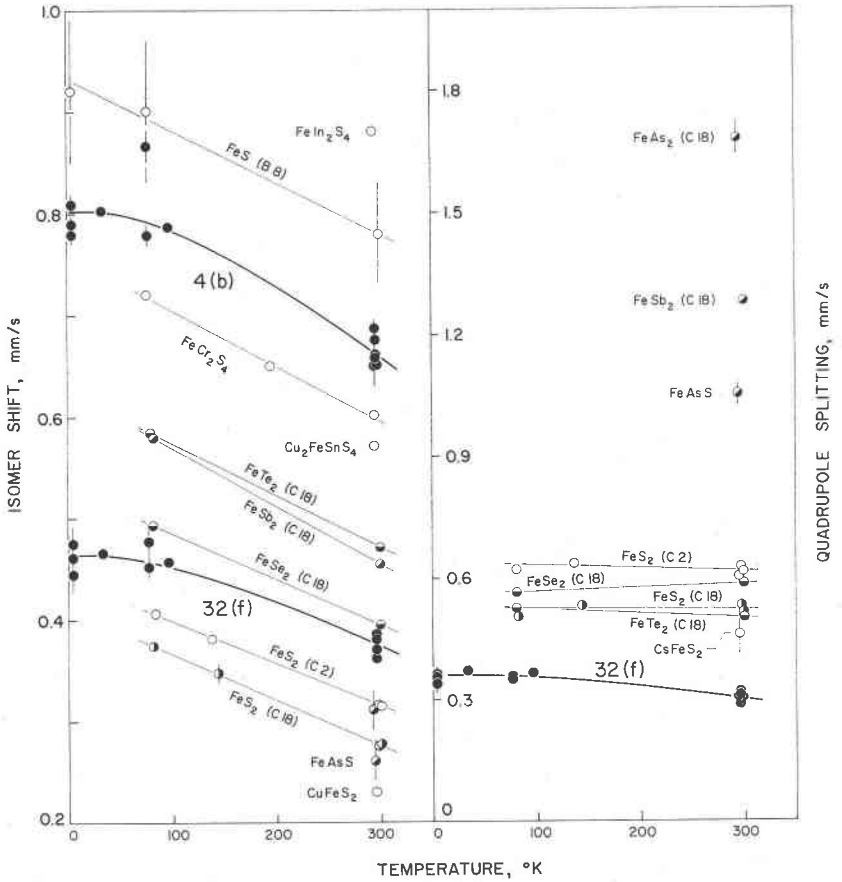

FIG. 2. Isomer shifts and quadrupole splittings of pentlandite (full circles) and related compounds. The isomer shifts are relative to metallic iron (converted where necessary). Temperley and Lefevre (1966): $FeS_2$ (*C*2 and *C*18), $FeSe_2$, $FeTe_2$, $FeSb_2$. Imbert *et al.* (1963): FeAsS, $FeAs_2$. Fluck *et al.* (1963): $FeS_2$ (*C*2 and *C*18). Hafner and Kalvius (1966): FeS. Greenwood and Whitfield (1968): $CuFeS_2$, $FeCr_2S_4$, $FeIn_2S_4$, $Cu_2FeSnS_4$. Raj and Puri (1969): $CsFeS_2$.

139–149 (77°K) and 140–144 (4.2°K) is $4.6 \pm 0.4$ for natural and $13.3 \pm 1.0$ for annealed pentlandite. The ratio 13.3/4.6 is $2.9 \pm 0.3$, which is very close to the weighted mean of the corresponding individual $R$(annealed)/$R$(natural) ratios for the four pairs, $3.0 \pm 0.4$. From $\bar{R} = 4.6 \pm 0.4$ one obtains Fe($b$) $= 3.0 \pm 0.3$ for natural pentlandite, while from $\bar{R} = 13.3 = 1.0$ the value of $1.2 \pm 0.1$ is obtained for Fe($b$) in annealed pentlandite. The number of iron atoms transferred from 4($b$) to 32($f$) on annealing is thus

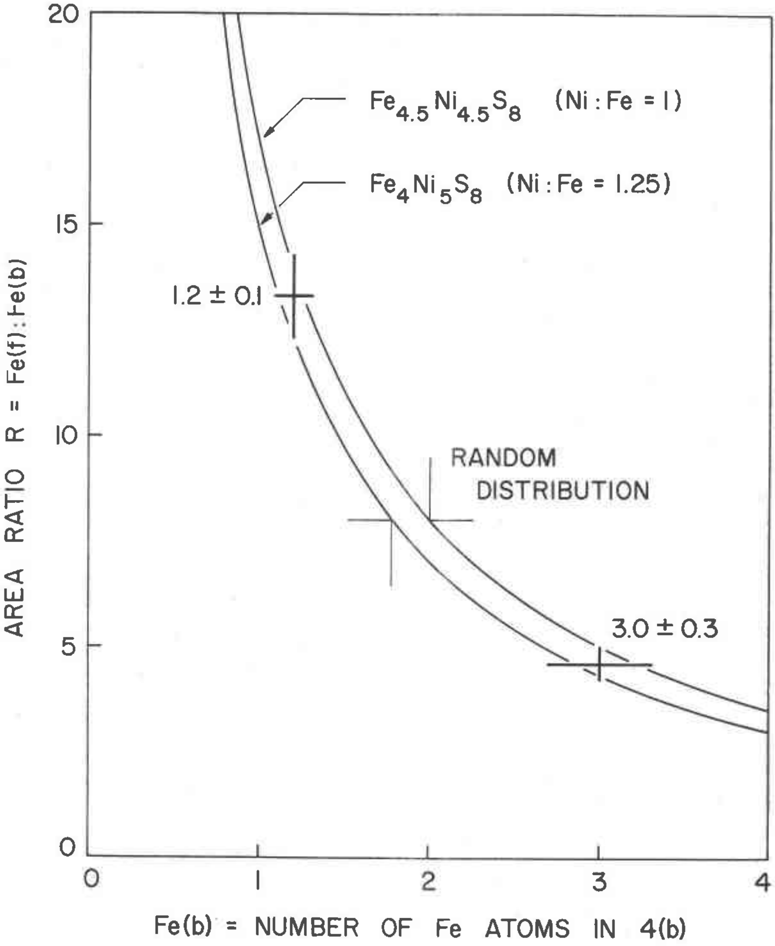

FIG. 3. Change in the number of Fe atoms, Fe(*b*), in the octahedral 4(*b*) sites in pentlandite on annealing. The Fe(*b*) value of 3.0±0.3 refers to natural, that of 1.2±0.1, to annealed pentlandite.

1.8±0.3. Variations in the composition of homogeneous natural pentlandite, and uncertainties in the analytical figures, do not affect these results in a critical way (Fig. 3).

For a completely random distribution of the Fe atoms over 4(*b*)+32(*f*) Fe(*b*) would be 1.89±0.11. Fe(*b*) of annealed pentlandite is, however, 0.7±0.2 smaller. Thus it appears that the annealing process results, not in a complete randomization of the metal atoms that might be expected, but in an incomplete ordering which is the opposite of that present in natural pentlandite, *i.e.* with fewer $Fe_b$ atoms than would correspond to a statistical distribution.

*Quadrupole Splitting and Isomer Shift.* The quadrupole splitting at the 32(*f*) site is small, characteristic of complex Fe compounds (Fluck *et al.*, 1963), and is consistent with the small trigonal distortion of the $FeS_4$ tetrahedra expected in pentlandite; refined $x$ and $u$ values for the analogous synthetic phases $Fe_4Ni_4RuS_8$ and $Fe_4Ni_4RhS_8$ have been reported to be only slightly larger than the corresponding ideal values, $\frac{1}{8}$ and $\frac{1}{4}$ respectively (Reid, 1968; Reid, Knop, and Sutarno).[1] The increase in the quadrupole splitting on cooling is attributed to a thermal contraction of the structure which increases the electric field gradient at the Fe nucleus. Both the small splitting and its small variation with temperature are evidence that the contribution to the electric field gradient from uncompensated electrons of the Fe atom is very small, if any.[2] By contrast, the splitting for tetrahedrally coordinated $Fe^{2+}$ in sphalerite and wurtzite has been reported to be 2.05 mm/s at 80°K and 0.80 mm/s at 300°K (Marfunin and Mkrtchyan, 1967).

It does not appear possible to determine the oxidation and spin states of the Fe atom in pentlandite unambiguously from the Mössbauer spectra alone. The room-temperature isomer shift at 4(*b*) is not too far from the isomer shifts of FeS, In[FeIn]$S_4$, and $FeSb_2S_4$, all of which contain octahedrally coordinated divalent iron, so that the ground state at 4(*b*) could be $d_\epsilon^4 d_\gamma^2$ (Figs. 2 and 4). The isomer shift is significantly below those of FeS and In[FeIn]$S_4$, which already are rather small for $Fe^{2+}$ in six-coordination, even when their large uncertainty limits are taken into account.[3] But it is still much closer to these sulfides than to the low-spin Fe(II) in pyrite and marcasite.[4] The increase in the shift with decreasing

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[1] The $x$ and $u$ values as determined by diffraction methods are averages over all the $FeS_4$ *and* $NiS_4$ tetrahedra in the crystal, while the quadrupole splitting is an average measure of the asymmetry of the local electric field at the Fe nulcei of the $FeS_4$ tetrahedra. See also footnote on p. 1135.

[2] Local distortions arising from the non-cooperative Jahn-Teller effect, when present, can account for appreciable quadrupole splittings. Cf. the observations by Tanaka *et al.* (1966) on the normal spinels $Fe^{2+}Cr_2O_4$ and $Fe^{2+}V_2O_4$ at temperatures above their static transition temperatures.

[3] Because of the considerable difference between the isomer shifts reported for $FeSb_2S_4$ there is no value in comparing this compound with pentlandite. Eibschütz *et al.* (1967b) give $0.63 \pm 0.02$ mm/s for (presumably synthetic) $FeSb_2S_4$, while the shift listed by Marfunin and Mkrtchyan (1967) for the mineral berthierite (formulated as $Fe^{2+}Sb_2S_4$) is 1.12 mm/s at 300°K and 1.19 mm/s at 80°K; the corresponding quadrupole splittings were 2.67 and 3.60 mm/s respectively.

[4] Walker *et al.* (1961) place the isomer shifts of the weakly paramagnetic pyrite and marcasite on the $3d^54s^x$ line, and close to $x=0$, of their correlation diagram. However, as

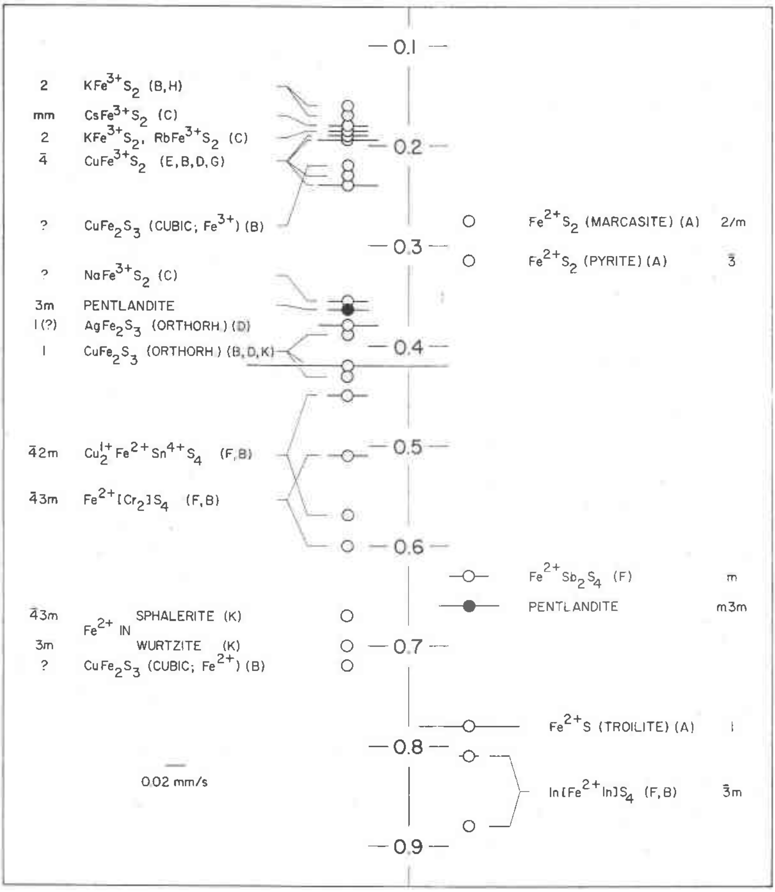

FIG. 4. Isomer shifts of octahedrally and tetrahedrally coordinated Fe$^{57}$ in sulfides at room temperature (in mm/s, relative to metallic iron). The experimental uncertainty, where stated, is indicated by horizontal stroke. Crystallographic site symmetries are also shown. The positive charges indicated in the formulae do not necessarily imply ionic state. *A*, see Fig. 2; *B*, Greenwood and Whitfield, 1968; *C*, Raj and Puri, 1969; *D*, Imbert and Wintenberger, 1967; *E*, Raj *et al.*, 1968; *F*, Eibschütz *et al.*, 1967a,b; *G*, Frank, 1968; *H*, Fluck *et al.*, 1963; *K*, Marfunin and Mkrtchyan, 1967.

temperature agrees with that expected from the second-order Doppler shift.

The quadrupole splitting at 4(*b*) and its temperature dependence shed

has already been noted by Marfunin and Mkrtchyan (1967) and by Erickson (1967), this is incompatible with the known physical properties of these sulfides which are more consistent with low-spin Fe(II) (Serres, 1953; Benoit, 1955; Hulliger and Mooser, 1965; Hulliger, 1968; Jarrett *et al.*, 1968; Gallagher *et al.*, 1969).

no light on the electronic configuration of the Fe atom. In an unperturbed ligand field of octahedral (*m3m*) symmetry the $d_\epsilon$ energy levels are degenerate and the sixth 3*d* electron of a high-spin $Fe^{2+}$ atom spends equal time in each of the $d_\epsilon$ orbitals (cf. Ingalls, 1962). The splitting will be nonzero only if the degeneracy is removed by an external perturbing field of lower symmetry. But it is not possible to decide from the spectra whether or not there is a quadrupole doublet at 4(*b*), as the evidence is statistically inconclusive and thus of no value for assigning the ground state. If a splitting *is* present, it is very small. By contrast, the quadrupole splitting at $Fe^{2+}$ in the inverse cubic spinel $In[FeIn]S_4$, in which the $FeS_6$ octahedra have the crystallographic symmetry $\bar{3}m$, is 3.27 mm/s (Greenwood and Whitfield, 1968). An example of $FeS_6$ octahedra containing low-spin Fe(III) does not seem to be available.

The isomer shift at $Fe_f$ is smaller than at $Fe_b$. This is not unexpected. The ligands are in both cases the same, and there is an increase in the *s*-character of the bonds passing from octahedral $sp^3d^2$ to tetrahedral $sp^3$ bonding orbitals. Hence a decrease in the isomer shift. Such decrease is commonly observed (cf. for example Edwards *et al.*, 1967; Greenwood and Whitfield, 1968) (Fig. 4).

According to a correlation diagram such as Erickson's Figure 2 (1967), the room-temperature isomer shift at $Fe_f$ would appear to fall in the overlap region of isomer shifts characteristic of low-spin Fe(II) and high-spin Fe(III). For further interpretation comparison must be made with isomer shifts observed in sulfides containing Fe in tetrahedral coordination.

The shift falls between that of $NaFeS_2$ and those of the orthorhombic minerals cubanite, $CuFe_2S_3$, and sternbergite, $AgFe_2S_3$ (Fig. 4). Its exact position with respect to the shifts in these sulfides, as well as with respect to stannite ($Cu_2FeSnS_4$) and $FeCr_2S_4$, is difficult to establish with accuracy because of the considerable experimental uncertainties and the discrepancies involved in comparing and converting results obtained by different authors. While there is reasonable evidence that the Fe atom is divalent in $FeCr_2S_4$ and stannite, and trivalent in $NaFeS_2$ and in the sulfides having room-temperature isomer shifts smaller than 0.3 mm/s (Fig. 4), the oxidation state of Fe in orthorhombic cubanite and in sternbergite has not been satisfactorily elucidated.

Greenwood and Whitfield (1968) have noted that in orthorhombic cubanite, in which all the Fe atoms are crystallographically equivalent, the isomer shift is midway between those of $Fe^{2+}$ in $FeCr_2S_4$ and $Fe^{3+}$ in $CuFeS_2$. They seem to suggest that this might lead to an expectation of separate six-line hyperfine Mössbauer spectra for both ferrous and ferric ions. Since only *one* six-line hyperfine spectrum was observed at both 295 and 77°K, they took this to imply that electrons were moving rapidly between $Fe^{2+}$ and $Fe^{3+}$ ions in the cubanite structure. However, they made no mention of relaxation line broadening that might be expected in mixed-valency compounds of iron; the room-temperature spectrum in their paper appears to consist of unbroadened lines. The room-temperature spectrum of the *cubic* cubanite obtained by heating the orthorhombic form above 270°C in vacuo, was not magnetically split.[1] Fitting of the broad composite line to two lines yielded separate isomer shifts for the ferric (0.22 mm/s) and ferrous (0.72 mm/s) components, and a ferric:ferrous area ratio of 1.15. An alternative fitting to a ferric singlet and a ferrous quadrupole doublet resulted in an isomer shift of 0.72 mm/s and a splitting of 0.20 mm/s for the ferrous component, leaving the ferric parameters virtually unaltered. It was concluded that there was no longer rapid interchange of the valencies in the disordered cubic phase as there had been in the orthorhombic phase.[2]

The similar six-line hyperfine spectrum of sternbergite obtained at 300, 77, and 4°K, on the other hand, was interpreted by Imbert and Wintenberger (1967) as being incompatible with the simultaneous existence of $Fe^{2+}$ and $Fe^{3+}$, with or without rapid exchange, on the grounds that such an exchange mechanism would cease to operate at low temperatures; 4°K was considered sufficiently low. The authors argued that the observed internal field was too weak for the Fe atom to be present as ferric ion, even though the magnitude of the isomer shift ($0.38 \pm 0.03$ mm/s at 300°K) and the $\frac{1}{2}e^2q_zQ$ term ($0.99 \pm 0.04$ mm/s, independent of temperature) are suggestive of such interpretation. They propose that a covalent or a metallic model be adopted to account for the properties of the antiferromagnetic sternbergite.

Clearly the electron delocalization that appears to exist in these sulfides complicates a simple interpretation in chemical (localized-electron) terms. The assignment of a clear-cut oxidation state, in the classical chemical sense, to the $Fe_f$ atoms undoubtedly poses a problem similar to that encountered in cubanite and sternbergite, and is probably not possible. It is well to keep in mind that there is a distinction between the oxidation state of the Fe atom and the electron density on the atom

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[1] This result is at variance with the observations of Makarov *et al.* (1968), who report a six-line hyperfine spectrum and conclude, from application of external fields, that the cubic modification at room temperature is anti-ferromagnetic.

[2] In $Fe_{1-x}Cu_xCr_2S_4$ ($0<x<0.5$) below the Curie temperature a double six-line spectrum was observed arising from both ferrous and ferric iron, but above the Curie temperature only a single line appeared. This was again explained on a fast relaxation between $Fe^{2+}$ and $Fe^{3+}$. For $0.5<x<1$ only $Fe^{3+}$ ions exist giving a single six-line spectrum below the Curie temperature (Haacke and Nozik, 1968).

(*cf.* for example Greenwood, 1967). However, the oxidation states of Fe in pentlandite, unlike those in the ferricyanide and ferrocyanide ions, are probably beyond the reach of determination by chemical means. It is hoped that the magnetic susceptibility measurements which are being initiated, and Mössbauer spectra now being obtained in external magnetic fields, may help to resolve the difficulty.

## CONCLUSIONS

Analysis of the Mössbauer spectra of natural and annealed Sudbury pentlandite has substantiated the view that the irreversible structure expansion which takes place on annealing, is caused by a redistribution of the Fe and Ni atoms between the 4(*b*) and 32(*f*) sites. The redistribution does not result in a complete randomization of the metal atoms over 4(*b*)+32(*f*). The number of Fe atoms in the octahedral 4(*b*) sites was found to be 3.0±0.3 before and 1.2±0.1 after annealing, while a statistical distribution over the two equipoints would require 1.89±0.11 Fe atoms. The annealing process thus seems to bring out a weak tendency of the Fe atoms to prefer the tetrahedral sites, or of the Ni atoms to prefer the octahedral sites, or both.

The isomer shift at the $Fe^{57}$ nucleus is significantly larger for the 4(*b*) site than for the 32(*f*) site. The quadrupole splitting at the 32(*f*) site is only about 0.3 mm/s and almost temperature independent. No evidence of magnetic ordering was observed in the spectra even on cooling the specimens to 4.2°K. To account for these results the iron in the $FeS_6$ octahedra is assumed to be divalent and involved in appreciable covalent bonding of the $sp^3d^2$ type. The Fe atom in the slightly distorted $FeS_4$ tetrahedron is engaged in appreciable covalent bonding of an essentially $sp^3$ type, but its ground state cannot be ascertained from the present Mössbauer evidence alone. This precludes meaningful answers from being given to questions like: What determines the site preference of the Fe atoms in natural and annealed pentlandite; Why does the lattice parameter of synthetic $\pi$(Fe, Ni, S) increase with the Fe:Ni ratio; What are the relative contributions to the quadrupole splitting at the $Fe_f$ nucleus from the ligand environment and from the asymmetry of the electron occupancy in the 3*d* orbitals; Can the quadrupole splitting be used to estimate, empirically, the degree of distortion of $FeS_4$ tetrahedra? Work to clarify some of these problems as they affect synthetic pentlandites and $\pi$(Fe, Co, Ni, S) phases is under way.

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## REFERENCES

BARKER, W. W. (1966) *Ternary Rare Earth Oxides.* Ph.D. Thesis. University of Western Australia, Nedlands, W. Austr.

———, AND O. KNOP (1970) Chalkogenides of the transition elements. VIII. A computer-simulation study of the metal-metal coordination in cubic $\pi$ phases, particularly in pentlandite, $Fe_{9-x}Ni_xS_8$. *Can. J. Chem.* in press.

BENOIT, RENÉ (1955) Etude paramagnétique des composés binaires. *J. Chim. Phys.* **52,** 119–132.

CLARK, P. E., A. W. NICHOL, AND J. S. CARLOW (1967) A precision velocity generator suitable for Mössbauer experiments. *J. Sci. Inst.* **44,** 1001–1004.

EDWARDS, P. R., C. E. JOHNSON, AND R. J. P. WILLIAMS (1967) Mössbauer spectra of some tetrahedral iron (II) compounds. *J. Chem. Phys.* **47,** 2074–2082.

EIBSCHÜTZ, M., E. HERMON, AND S. SHTRIKMAN (1967a) Magnetic susceptibility and Mössbauer effect measurements in $FeIn_2S_4$. *Solid State Commun.* **5,** 529–531.

———, ———, AND ——— (1967b) Determination of cation valencies in $Cu_2Fe^{57}Sn^{119}S_4$ by Mössbauer effect and magnetic susceptibility measurements. *J. Phys. Chem. Solids,* **28,** 1633–1636.

ERICKSON, N. E. (1967) Mössbauer spectroscopy of iron compounds. *Advan. Chem. Ser.* **68,** 86–104. American Chemical Society, Washington, D.C.

FLUCK, E., W. KERLER, AND W. NEUWIRTH (1963) The Mössbauer effect and its significance in chemistry. *Angew. Chem. Int. Ed.* **2,** 277–287.

FRANK, E. (1968) Comments on the interpretation of Mössbauer effect data in chalcopyrite. *Nuovo Cimento B,* **58,** 407–412.

GALLAGHER, P. K., J. B. MACCHESNEY, AND R. C. SHERWOOD (1969) Mössbauer effect in the system $Co_{1-x}Fe_xS_2$. *J. Chem. Phys.* **50,** 4417–4419.

GREENWOOD, N. N. (1967) General discussion. *Symp. Farad. Soc. No. 1 (The Mössbauer Effect),* p. 47–49.

———, AND H. J. WHITFIELD (1968) Mössbauer effect studies on cubanite ($CuFe_2S_3$) and related iron sulphides. *J. Chem. Soc., A,* **1968,** 1697–1699.

HAACKE, G., AND A. J. NOZIK (1968) Mössbauer effect in $Fe_{1-x}Cu_xCr_2S_4$. *Solid State Commun.* **6,** 363–365.

HAFNER, STEFAN, AND MICHAEL KALVIUS (1966) The Mössbauer resonance of $Fe^{57}$ in troilite (FeS) and pyrrhotite ($Fe_{0.88}S$). *Z. Kristallogr.* **123,** 443–458.

HULLIGER, F. (1968) Crystal chemistry of the chalcogenides and pnictides of the transition elements. *Struct. Bonding,* **4,** 83–229.

———, AND E. MOOSER (1965) Semiconductivity in pyrite, marcasite and arsenopyrite phases. *J. Phys. Chem. Solids,* **26,** 429–433.

IMBERT, PIERRE, ANDRÉ GÉRARD, AND MICHELINE WINTENBERGER (1963) Etude des sulfure, arséniosulfure et arséniure de fer naturels par effect Mössbauer. *C. R. Acad. Sci. Paris* **256,** 4391–4393.

———, AND M. WINTENBERGER (1967) Etude des propriétés magnétiques et des spectres d'absorption par effect Mössbauer de la cubanite et de la sternbergite. *Bull. Soc. Fr. Mineral. Cristallogr.* **90,** 299–303.

INGALLS, R. (1962) Variational calculation of the Sternheimer factors for the ferrous ion. *Phys. Rev.* **128,** 1155–1158.

KNOP, OSVALD, AND MOHAMMAD ANWAR IBRAHIM (1961) Chalkogenides of the transition elements. II. Existence of the π phase in the $M_9S_8$ section of the system Fe-Co-Ni-S. *Can. J. Chem.* **39,** 297–317.

———, ———, AND SUTARNO (1965) Chalkogenides of the transition elements. IV. Pentlandite, a natural π phase. *Can. Mineral.* **8,** 291–324.

———, K. I. G. REID, SUTARNO, AND YASUAKI NAKAGAWA (1968) Chalkogenides of the transition elements. VI. X-ray, neutron and magnetic investigation of the spinels $Co_3O_4$, $NiCo_2O_4$, $Co_3S_4$, and $NiCo_2S_4$. *Can. J. Chem.* **46,** 3463–3476.

MAKAROV, E. F., A. S. MARFUNIN, A. R. MKRTCHYAN, V. A. POVITSKII, AND R. A. STUKAN (1968) Investigation of the magnetic ordering of $CuFe_2S_3$ by gamma resonance (Mössbauer) spectroscopy. *Fiz. Tverd. Tela,* **10,** 913–915 [(Eng. transl.) *Soviet Phys.—Solid State,* **10,** 717–718].

MARFUNIN, A. S., AND A. R. MKRTCHYAN (1967) Mössbauer spectra of $Fe^{57}$ in sulfides. *Geokhim.* No. 10, 1094–1103; [(Engl. transl.) *Geochemistry Internat.* **4,** 980–989.]

MUIR, ARTHUR H., JR., KEN J. ANDO, AND HELEN M. COOGAN (1967) *Mössbauer Effect Data Index, 1958–1965.* Interscience, New York, P. 26.

OKIJI, AYAO, AND JUNJIRO KANAMORI (1964) Theoretical analysis of the Mössbauer data in some $Fe^{2+}$ compounds. *J. Phys. Soc. Japan,* **19,** 908–915.

ÔNO, KAZUO, ATSUKO ITO, AND EIJI HIRAHARA (1962) Mössbauer study of $FeS_{1.00}$, $FeS_{1.05}$ and $FeS_{1.07}$. *J. Phys. Soc. Japan,* **17,** 1615–1620.

PRESTON, R. S., S. S. HANNA, AND J. HEBERLE (1962) Mössbauer effect in metallic iron. *Phys. Rev.* **128,** 2207–2218.

RAJ, DEO, K. CHANDRA, AND S. P. PURI (1968) Mössbauer studies of chalcopyrite. *J. Phys. Soc. Japan,* **24,** 39–41.

RAJ, DEO, AND S. P. PURI (1969) Mössbauer spectra of tetrahedral alkali dithioferrates (III). *J. Chem. Phys.* **50,** 3184–3190.

REID, K. I. G. (1968) *X-Ray Studies of Transition Metal Chalkogenides.* Ph.D. Thesis. Dalhousie University, Halifax, N.S.

SERRES, A. (1952) Sur quelques composés du cobalt et du fer à paramagnétisme très faible et constant. *J. Phys. Radium,* **14,** 689–690.

TANAKA, MIDORI, TETSUZI TOKORO, AND YOSHIMICHI AIYAMA (1966) Jahn-Teller effects on Mössbauer spectra of $Fe^{57}$ in $FeCr_2O_4$ and $FeV_2O_4$. *J. Phys. Soc. Japan,* **21,** 262–267.

TEMPERLEY, A. A., AND H. W. LEFEVRE (1966) The Mössbauer effect in marcasite structure iron compounds. *J. Phys. Chem. Solids,* **27,** 85–92.

WALKER, L. R., G. K. WERTHEIM, AND V. JACCARINO (1961) Interpretation of the $Fe^{57}$ isomer shift. *Phys. Rev. Lett.* **6,** 98–101.

WOODHAMS, F. W. D., J. S. CARLOW, AND R. E. MEADS (1966) A simple temperature control system for use between 4.2°K and room temperature. *J. Sci. Inst.* **43,** 333–334.

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