American Mineralogist, Volume 65, pages 157–162, 1980

^{57}Fe Mössbauer study of babingtonite

GEORG AMTHAUER[1]

Institut für Mineralogie, Universität Marburg
Lahnberge, 3550 Marburg/Lahn, F. R. Germany

Abstract

The Mössbauer spectra of ^{57}Fe in babingtonite were taken between 30 K and 600 K. Two doublets were observed and assigned to octahedral Fe^{2+} and Fe^{3+} in distinct crystallographic sites. Mn^{2+} appears to substitute for Fe^{2+}. No evidence of delocalized electrons can be observed in the Mössbauer spectra even though the Fe^{2+} and Fe^{3+} oxygen octahedra share common edges in this structure. Quadrupole splittings and isomer shifts of both doublets reveal no great changes of the crystallographic and electronic structure between 30 and 600 K.

Introduction

Babingtonite is a chain silicate with the chemical formula $Ca_2(Fe^{2+},Mn,Mg)Fe^{3+}Si_5O_{14}OH$. According to Araki and Zoltai (1972), babingtonite is triclinic with the space group $P\bar{1}$. Recently Kosoi (1976) reinvestigated the structure and determined the space group to be $P1$. Although the principal topology is very similar, the two papers present different settings of the structure and therefore different cell constants, atomic positions, and distances.

There are two chains of SiO_4 tetrahedra (5 tetrahedra per repeat unit) parallel to [110] (Araki and Zoltai) or to [100] (Kosoi). According to Araki and Zoltai, these chains are connected by two crystallographic distinct FeO_6 octahedra differing in the degree of distortion and in the average cation–anion distance. The average Fe–O distance is 2.1687A in the Fe(1) octahedron and 2.0477A in the Fe(2) octahedron, indicating that the former is mainly occupied by Fe^{2+} and the latter by Fe^{3+}. Kosoi reports similar results. The Ca atoms are also located in two different sites in the large openings between the chains and the Fe octahedra.

The chemical formula shows that cations other than those of the pure Ca–Fe silicate can enter the babingtonite structure. The most important of these ions seems to be Mn, with some chemical analyses reporting more than 1.0 weight percent MnO. The assumption of one Fe^{2+} and one Fe^{3+} site is supported by the room-temperature Mössbauer spectrum of babingtonite presented by Araki and Zoltai, which indicates a simple pattern of separated single peaks for Fe^{2+} and Fe^{3+} at high velocities. No other Mössbauer study of babingtonite has been published.

The present study is part of a detailed spectroscopic investigation of minerals bearing Fe^{2+} and Fe^{3+} in adjacent sites, in order to study possible interactions of these ions and their spectral features. This paper reports a Mössbauer investigation of babingtonite at temperatures between 30 and 600 K in order to study:

(1) The resolution of the spectra and the behavior of the spectral parameters at different temperatures.
(2) The cation distribution and the substitution of Mn in babingtonite.
(3) Possible electron exchange between Fe^{2+} and Fe^{3+} similar to that found by the Mössbauer effect in other mineral such as magnetite (Bauminger *et al.*, 1967), ilvaite (Gerard and Grandjean, 1971), and the hematite–ilmenite series (Warner *et al.*, 1972).

Experimental methods

The Mössbauer spectra were taken using conventional techniques (^{57}Co/Rh source, symmetric triangular velocity wave form, 512 channels per spectrum; 5 mg Fe/cm^2 absorber density, refrigerator cryostat, vacuum furnace). Details of the experimental apparatus are reported in Amthauer *et al.* (1976). Chemical analyses were obtained with a MAC5-SA3 electron microprobe, using the method of Bence and Albee (1968) for data reduction. The total iron was

---

[1] Present address: California Institute of Technology, Division of Geological and Planetary Sciences, Pasadena, California 91125.

0003–004X/80/0102–0157$02.00

determined with the microprobe as FeO; the Fe^{2+}/Fe^{3+} ratio was evaluated from the Mössbauer spectra.

Results

The chemical composition of the samples and their localities are reported in Table 1. Two babingtonites were studied. The one from Herbornseelbach, Hessen, Germany occurs together with quartz and calcite in cavities in a massive ferruginous quartzite. The Hampden County, Massachusetts babingtonite is found together with quartz and calcite at the Lane trap-rock quarry near Westfield (Smithsonian Institution, catalog #NMNH120676).

Figure 1 shows the Mössbauer spectrum of the Westfield babingtonite taken at room temperature. Three peaks are resolved, which can be explained on the basis of two doublets, whose low-velocity components strongly overlap. This interpretation is supported by several data. Figure 2 shows the spectra taken at 30 and at 525 K. In both spectra four peaks are resolved and two doublets could easily be fitted without any constraints. The resolution of the low-velocity peak into two components starts at 425 K going to high temperatures and at 150 K going to low temperatures. Below 30 K the spectrum reveals the beginning of magnetic ordering. Between 200 and 375 K the fit was started with two doublets, and the areas of the high- and the low-velocity peaks of each doublet were set to be equal. During the final fitting procedure these constraints were removed without changing the parameters significantly. Nevertheless, both doublets were found to be essentially area symmetric, and at room temperature the area of the unresolved low-velocity peaks is equal to the sum of the areas of the two high-velocity peaks.

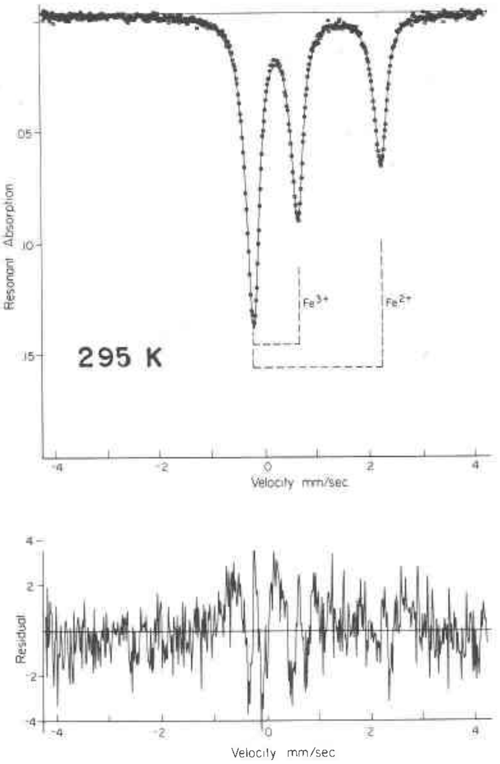

Fig. 1. Mössbauer spectrum of ^{57}Fe in babingtonite at room temperature. The deviation of the solid line from the data divided by the square root of the background (=residual) is plotted below the spectrum.

Table 1. Chemical composition (wt%) of the babingtonites

Sample	1	2
Na_2O	.03	.02
K_2O	.01	.00
CaO	19.83	19.74
MgO	.88	.74
MnO	1.29	2.81
FeO	9.33	8.24
Fe_2O_3	13.03	13.51
Al_2O_3	.68	.64
Cr_2O_3	.03	.02
TiO_2	.01	.03
SiO_2	53.20	53.38
Total	98.32	99.13

1 = babingtonite from Westfield, Massachusetts
2 = babingtonite from Herbornseelbach, West Germany

Figures 1 and 2 show that the two doublets differ in intensity. The lower-intensity doublet has larger quadrupole splittings and isomer shifts than the high-intensity doublet. At low temperatures the low-velocity component of the weaker doublet is located at the most negative velocity, whereas at high temperatures this situation is reversed. Quadrupole splittings QS, isomer shifts IS, peak-widths Γ, and the relative areas A of both doublets at temperatures between 30 and 575 K are reported in Table 2. The fits are reasonably good as indicated by the χ^2. The quadrupole splittings and the isomer shifts of both doublets are plotted as function of temperature in Figure 3 and Figure 4 respectively. Room-temperature spectra taken before and after the heating experiments revealed no significant differences of the spectral parameters and particularly the Fe^{2+}/Fe^{3+} ratio.

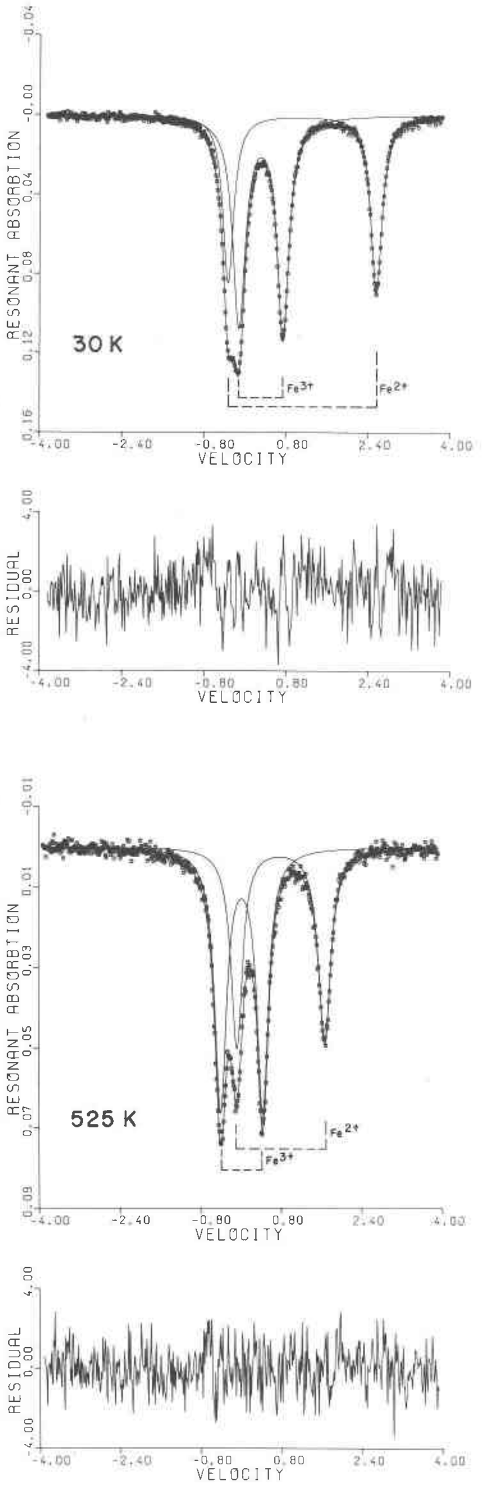

Fig. 2. Mössbauer spectrum of ^{57}Fe in babingtonite at 525 K (lower spectrum) and 30 K (upper spectrum). The deviation of the solid line from the data divided by the square root of the background (=residual) is plotted below the spectrum. Two doublets are fitted to the data.

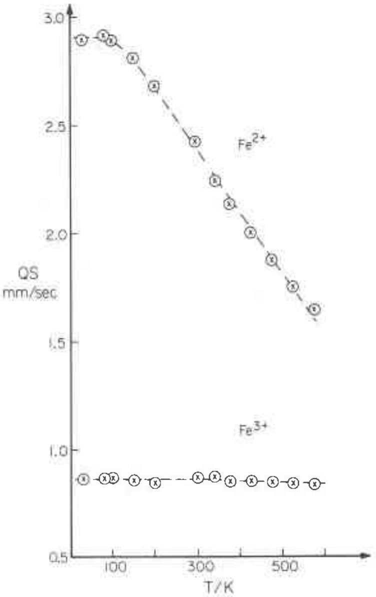

Fig. 3. Plot of the Fe^{2+} and Fe^{3+} quadrupole splittings QS in babingtonite against the temperature *T*.

Interpretation and discussion

Assignment of the doublets

The spectral features reported in the previous section are consistent with the assignment of the doublet with the smaller quadrupole splitting and the lower isomer shift to Fe^{3+} and the assignment of the other doublet to Fe^{2+}. Both Fe ions are in the high spin state. The strong temperature-dependence of the Fe^{2+} quadrupole splitting is in agreement with that assignment, as is the nearly complete invariance of the Fe^{3+} quadrupole splitting with temperature (*cf.* Fig. 3). The isomer shift of the Fe^{2+} doublet (IS = 1.18 mm/sec at 295 K, and 1.31 mm/sec at 80 K) is within the range of isomer shifts of Fe^{2+} in sixfold coordinated sites in silicates, *e.g.* in the M1 position (IS = 1.17 mm/sec at 295 K, and 1.29 mm/sec at 77 K) and M2 position (IS = 1.13 mm/sec at 295 K, and 1.26 mm/sec at 77 K) in orthopyroxene (Burnham *et al.*, 1971), indicating that Fe^{2+} also fills 6-fold coordinated sites in babingtonite. The isomer shift of the Fe^{3+} doublet (IS = 0.38 mm/sec at 295 K and 0.51 mm/sec at 80 K) may be compared with those of Fe^{3+} at the octahedral positions in garnets (IS = 0.36–0.41 mm/sec at 295 K, and 0.45–0.50 mm/sec at 77 K; Amthauer *et al.*, 1976).

The small line width of each doublet within the entire temperature range indicates that only one Fe^{2+} and one Fe^{3+} doublet is present rather than overlap

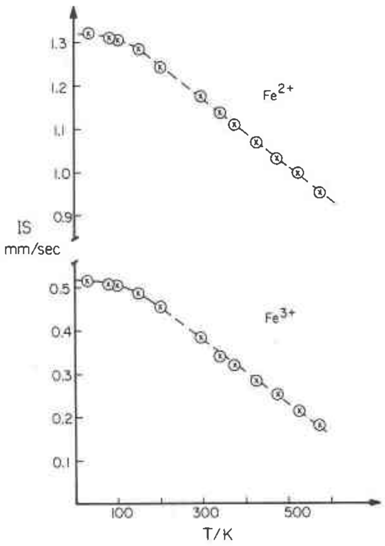

Fig. 4. Plot of the Fe^{2+} and Fe^{3+} isomer shifts IS in babingtonite against the temperature *T*.

of several Fe^{3+} and Fe^{2+} doublets. No additional absorption features can be observed within the temperature range, which shows that both iron atoms occupy distinct positions and are ordered. With respect to the results of the crystal structure refinements (Araki and Zoltai, 1972; Kosoi, 1976) it is most probable that Fe^{2+} occupies the so-called Fe(1) sites with the larger average cation–anion distance of 2.15–2.17A and Fe^{3+} the so-called Fe(2) sites with the smaller average cation–anion distance of 2.04–2.05A. The relatively high distortion of the Fe(2) or Fe^{3+} site found by Araki and Zoltai is reflected in a larger quadrupole splitting of Fe^{3+} in babingtonite (QS = 0.84–0.88 mm/sec), compared to the quadrupole splitting of octahedral Fe^{3+} in garnets (QS = 0.32–0.75 mm/sec; Amthauer *et al.*, 1976), or of octahedral Fe^{3+} in orthopyroxene (QS = 0.70–0.73 mm/sec; Annersten *et al.*, 1978). The differences between the Mössbauer paramaters of the two babingtonite samples taken at room temperature are within the experimental error, except for the areas.

Cation distribution and crystal chemical formula

All the spectra reveal that the areas of the Fe^{2+} and Fe^{3+} doublets are not equal, as would be the case for an ideal babingtonite composition with both Fe(1) and Fe(2) sites filled completely with iron. This deviation can be understood by considering that additional cations like Mn, Mg, Na, *etc.* are present in the samples. However, the question of possible different recoil-free fractions must be considered. Theoretically, these should be unequal for Fe^{2+} and Fe^{3+} at different crystallographic positions, as is observed for Fe^{2+} at the dodecahedral and Fe^{3+} at the octahedral positions in garnets (Whipple, 1973; Amthauer *et al.*, 1976); practically these differences are often within the error of the measurements and can be neglected.

The variations of the relative Fe^{2+} and Fe^{3+} areas with temperature in the spectra of the Westfield babingtonite are within the experimental error (*cf.* Table 2). This can be regarded as an indication of negligibly small differences of the recoil-free fractions of both Fe ions at their distinct lattice sites. Nevertheless, the Debye or Mössbauer temperatures θ_i of Fe^{2+} and Fe^{3+} in babingtonite were determined from the temperature-dependence of the areas A_i or recoil-free fractions f_i by the procedure of Herber *et al.* (1978). Details of the evaluation procedure as well as the crystallographic aspects of different θ_i in various silicates and other inorganic compounds will be discussed in more detail in a forthcoming paper by Scheringer and Amthauer (in preparation). In babingtonite $\theta_{Fe^{2+}}$ was found to be 320±20 K and $\theta_{Fe^{3+}}$ to be 350±20 K. Thus, with the known θ_i one can calculate the relative recoil-free fractions f_i or the rela-

Table 2. ^{57}Fe Mössbauer parameters in babingtonite at different temperatures

Nr^a	T K	Fe^{2+} QS^b	IS^c	Γ	A^e	Fe^{3+} QS^b	IS^c	Γ	A^e	χ^2
1	30	2.89	1.32	0.26	44.3	0.86	0.51	0.29	55.7	729
1	80	2.91	1.31	0.26	44.1	0.86	0.51	0.29	55.8	679
1	100	2.89	1.31	0.27	44.1	0.86	0.50	0.29	55.9	615
1	150	2.81	1.28	0.29	44.4	0.85	0.49	0.30	55.6	608
1	200	2.68	1.24	0.28	44.6	0.84	0.45	0.29	55.4	647
1	295	2.42	1.18	0.29	44.3	0.88	0.38	0.28	55.7	646
1	340	2.24	1.14	0.29	44.3	0.87	0.34	0.27	55.7	597
1	375	2.14	1.11	0.28	44.0	0.86	0.32	0.26	56.0	593
1	425	2.01	1.07	0.30	44.6	0.85	0.28	0.27	55.4	515
1	475	1.87	1.03	0.29	44.1	0.85	0.25	0.28	55.9	603
1	525	1.75	0.99	0.28	42.9	0.84	0.22	0.28	57.1	563
1	575	1.65	0.96	0.29	42.9	0.84	0.18	0.28	57.1	519
2	295	2.43	1.19	0.28	40.4	0.87	0.40	0.29	59.6	679

a sample Nr: 1 = sample from Westfield, Massachusetts
2 = sample from Herbornseelbach, Germany
b QS = quadrupole splitting in mm/sec ± 0.01 mm/sec
c IS = isomer shift referred to α-iron at room temperature in mm/sec ± 0.01 mm/sec
d Γ = full width at half peak height in mm/sec ± 0.01 mm/sec
e A = area in % referred to the total resonant absorption area = 100% (standard error ±2.00%)

tive areas A_i for Fe^{2+} and Fe^{3+}. If we assume that Fe^{2+} and Fe^{3+} occupy completely their sites, then $Fe^{2+}/(Fe^{2+} + Fe^{3+}) = 48.4\%$ and $Fe^{3+}/(Fe^{2+} + Fe^{3+}) = 51.0\%$ at 295 K. This is nearly within the experimental error, which is ±2.0%. In detail the area of Fe^{2+} is distinctly lower than calculated and also different in the two samples (*cf.* Table 2). This can be explained by a partial substitution of Fe^{2+} and to a minor amount also of Fe^{3+} by other cations such as Mn, Mg, Al.

The amount of cations is very similar in both samples except for Fe^{2+} and Mn^{2+}. The number of the Si, Ca, and Fe^{3+} ions on the basis of 14 oxygens and one hydroxyl ion is very close to the ideal values of 5, 2, and 1 respectively, whereas there is a distinct deficit of cations at the Fe^{2+} position. Therefore I conclude that, as in other silicates, Mg and Mn enter the Fe^{2+} sites. On the basis of 29 negative charges most of the Mn must also be divalent. Thus, the following chemical formulas for both samples can be postulated:

Herbornseelbach:

$Ca_{1.99}[Fe^{2+}_{0.65}Mg_{0.11}Mn^{2+}_{0.22}][Fe^{3+}_{0.95}Al_{0.07}]Si_{5.01}O_{14}OH$

Westfield:

$Ca_{2.01}[Fe^{2+}_{0.74}Mg_{0.13}Mn^{2+}_{0.10}][Fe^{3+}_{0.93}Al_{0.06}]Si_{5.02}O_{14}OH$

Elements present in wt% <0.01, *e.g.* Na, K, Cr, and Ti (*cf.* Table 1) were omitted in the calculation of the chemical formulas.

Chemical bonding and crystal structure

The values of the isomer shifts of both Fe ions are close to those found for Fe^{2+} and Fe^{3+} in other silicates, which indicates normal Fe–O bonds. This conclusion is supported by the temperature-dependence of the isomer shift, which is found to be nearly linear above 200 K for both Fe^{2+} and Fe^{3+}. $D(IS)/dT$ is $-(7.68\pm.02) \times 10^{-4}$ for Fe^{2+} and $-(7.25\pm.02) \times 10^{-4}$ mm/sec K for Fe^{3+} and is near to the theoretical value of -7.32×10^{-4} mm/sec K caused by the second-order Doppler shift (Amthauer *et al.,* 1976). This indicates no change of the chemical bonding with increasing temperature.

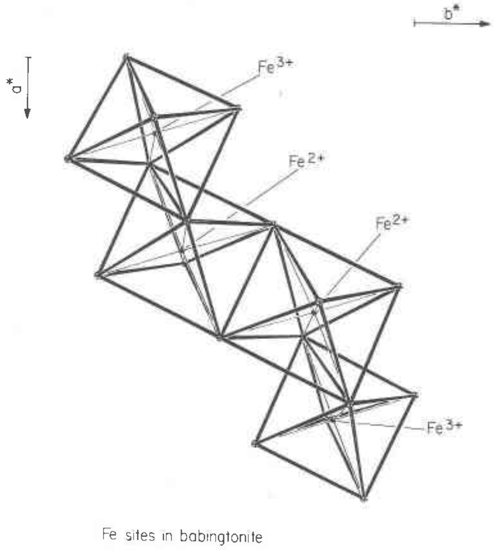

Fig. 5. Projection of the Fe–O octahedra in babingtonite onto the plane a*b*.

In Figure 5 a computer projection (Johnson, 1965) of the Fe octahedra of one unit cell on the a*b* plane is shown, using the data of Araki and Zoltai (1972). One can observe two Fe^{3+} and two Fe^{2+} octahedra which are connected by common edges showing the sequence Fe^{3+}–Fe^{2+}–Fe^{2+}–Fe^{3+}. The Fe^{3+}–Fe^{2+} distance is 3.296A; the Fe^{2+}–Fe^{2+} distance is 3.375A. This first distance is close to the upper limit of Fe–Fe distances (3.25A) reported for minerals showing electron exchange (Loeffler *et al.,* 1975). Nevertheless, in contrast to the optical and near infrared absorption spectra recently studied by Amthauer and Rossman (in preparation), the Mössbauer spectra reveal no resonant absorption features which could be attributed to electron exchange or hopping between Fe^{2+} and Fe^{3+}, although these two ions are located in neighboring octahedra sharing common edges. The amount of delocalized electrons, if any, must be very small and below the detectibility of the Mössbauer effect. This can be partly explained on the basis of the crystal structure. Only the four Fe atoms shown in Figure 5 are connected by common edges and there is no further edge-shared connection to the FeO_6 octahedra of other unit cells, and no infinite FeO_6 chain can be observed as in some other silicates (*i.e.,* ilvaite). In addition, Fe^{2+} and Fe^{3+} occupy distinct crystallographic positions with different potential energies, unlike magnetite and ilvaite, where electron exchange is known to occur between Fe^{2+} and Fe^{3+} occupying crystallographically equivalent sites. It cannot be totally excluded that in other babingtonites Fe^{2+} and Fe^{3+} are partially disordered over the Fe sites or even the Ca sites—as perhaps in samples formed at high temperatures—and as a result the extent of electron delocalization may be larger. On the other hand, charge transfer or electron hopping features in the optical absorption spectra may not necessarily be observed in the Mössbauer spectra, because in the optical absorption experiment the energy for the intervalence transition is supplied by the incident light, whereas the delocalization of electrons requires thermal activation. In addition, these thermally delocalized electrons can only be observed in the Mössbauer experiment if the exchange rate of an electron between Fe^{2+} and Fe^{3+} in adjacent lattice sites is faster than the mean lifetime of the excited Fe nucleus. Nevertheless, from the results of this investigation babingtonite has to be classified as a type I mixed valence compound (Robin and Day, 1967), revealing mainly the spectroscopic properties of the individual Fe atoms. Furthermore, this study provides a whole set of Mössbauer data as function of temperature for Fe^{2+} and Fe^{3+} in a more or less "ionic" state, which may be used for comparison and the interpretation of more complicated Mössbauer spectra such as deerite (Amthauer, in preparation).

Acknowledgments

I thank S. Hill (Pasadena) for performing the microprobe analysis, N. Runge (Marburg) for his assistance in fitting the spectra, and S. Hafner (Marburg) for use of the Mössbauer equipment. The sample from Herborn was kindly supplied by R. Helmbold, Mineralogisches Museum der Universität Marburg, the sample from Westfield, Massachusetts by J. S. White, Smithsonian Institution, Washington. The manuscript has been critically reviewed by H. Annersten (Uppsala), W. Dollase (Los Angeles), G. Rossman (Pasadena), F. Seifert (Kiel), and T. Zoltai (Minnesota).

References

Amthauer, G., H. Annersten and S. S. Hafner (1976) The Mössbauer spectrum of ^{57}Fe in silicate garnets. *Z. Kristallogr., 143,* 14–55.

Annersten, H., M. Olesch and F. A. Seifert (1978) Ferric iron in orthopyroxene: a Mössbauer spectroscopic study. *Lithos, 11,* 301–310.

Araki, T. and T. Zoltai (1972) Crystal structure of babingtonite. *Z. Kristallogr., 135,* 355–375.

Bauminger, R., S. G. Cohen, A. Marinov, S. Ofer and E. Segal (1961) Study of the low-temperature transition in magnetite and the internal fields acting on iron nuclei in some spinel ferrites using Mössbauer absorption. *Phys. Rev., 122,* 1447–1450.

Bence, A. E. and A. L. Albee (1968) Empirical correction factors for the electron microanalysis of silicates and oxides. *J. Geol., 76,* 382–403.

Burnham, C. W., Y. Ohashi, S. S. Hafner and D. Virgo (1971) Cation distribution and atomic thermal vibrations in an iron-rich orthopyroxene. *Am. Mineral., 56,* 850–876.

Gerard, A. and F. Grandjean (1971) Observation by Mössbauer effect of an electron hopping process in ilvaite. *Solid State Comm., 9,* 1845–1849.

Herber, R. H. A. E. Smelkinson, M. J. Sienko and L. F. Schneemeyer (1978) Lattice dynamics in covalent solids: Sn in $SnS_{2-x}Se_x (0 \leq x < 2)$. *J. Chem. Phys., 68,* 3705–3712.

Johnson, C. K. (1965) *ORTEP:FORTRAN thermal ellipsoid plot program for crystal structure illustrations.* Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Kosoi, A. L. (1976) The structure of babingtonite. *Sov. Phys. Crystallogr., 20,* 446–451.

Loeffler, B. M., R. G. Burns and J. A. Tossell (1975) Metal–metal charge transfer transitions: interpretations of visible-region spectra of the moon and lunar materials. *Proc. 6th Lunar Sci. Conf.,* 2663–2676.

Robin, M. B. and P. Day (1967) Mixed valence chemistry—a survey and classification. *Adv. Inorg. Chem. Radiochem., 10,* 247–423.

Warner, B. N., P. N. Shive, J. L. Allen and C. Terry (1972) A study of the hematite–ilmenite series by the Mössbauer effect. *J. Geomag. Geoelectr., 24,* 353–367.

Whipple, E. R. (1973) *Quantitative Mössbauer Spectra and Chemistry of Iron.* Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Manuscript received, May 14, 1979;
accepted for publication, September 13, 1979.