

A MÖSSBAUER EFFECT STUDY OF TRIPLITE AND RELATED MINERALS

EDWARD KOSTINER,¹ *Baker Laboratory of Chemistry Cornell University
Ithaca, New York 14850*

ABSTRACT

Mössbauer parameters are reported for the phosphate minerals triplite, zwieselite, triploidite, and wolfeite. Analysis of the absorption data confirms the existence of non-equivalent ferrous ions. The broadening of the resonance peaks is rationalized on the basis of a microscopic disorder due to half-occupied fluorine sites in the fluoride minerals and to sets of closely related metal sites in the hydroxy minerals.

INTRODUCTION

Recently the crystal structures of triplite (Waldrop, 1969) and triploidite (Waldrop, 1970), two related phosphate minerals, have been determined. This paper reports the ⁵⁷Fe Mössbauer effect spectroscopy of triplite and three related minerals—zwieselite, wolfeite, and triploidite.

EXPERIMENTAL

The mineral samples were generously supplied by L. Waldrop. A description of each follows.

Triplite—(Mn,Fe)₂PO₄F, from Mica Lode pegmatite, Eight Mile Park, Fremont County, Colorado, Mn_{0.95}Fe_{0.25}—Mg_{0.7}Ca_{0.1}PO₄F. Composition and mineralogy described by Heinrich (1951). The crystal structure is monoclinic with two equally populated metal sites *M*(1) and *M*(2), each octahedrally coordinated by four oxygen and two fluorine atoms. The occupancy of the two metal sites is (Waldrop, 1969)



Zwieselite—(Fe,Mn)₂PO₄F, from Zwiesel, Bavaria. Described in Palache *et al.* (1944), p. 851. The atomic ratio of iron to manganese is 2.00; trace amounts of calcium and magnesium are present. Precession photographs show these specimens to be isotopic with triplite (Waldrop, 1970).

Triploidite—(Mn,Fe)₂PO₄OH, from Branchville, Connecticut. Described in Palache *et al.* (1944), p. 853. The crystal structure is related to that of triplite, with the *b*-axis doubled. There are a total of eight metal atom sites, belonging to two very similar groups of four octahedral and four trigonal bipyramidal atoms (Waldrop, 1970).

Wolfeite—(Fe,Mn)₂PO₄OH, from Palermo pegmatite, North Groton, New

¹Present address: Department of Chemistry, University of Connecticut, Storrs, Connecticut 06268.

Hampshire. Described by Frondel (1949); the iron to manganese ratio is 3.39. Precession photographs show the specimen to be isotypic with triploidite (Waldrop, 1970).

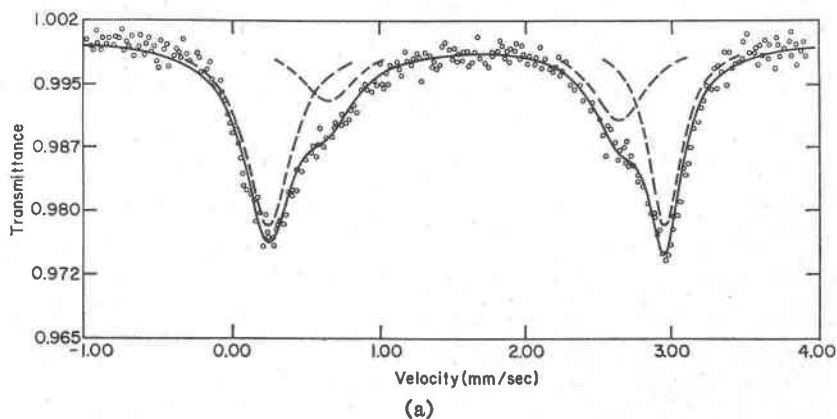
The room temperature ^{57}Fe Mössbauer effect was measured with a Model NS-1 Mössbauer Spectrometer (Nuclear Science and Engineering Corporation, Pittsburgh, Pennsylvania) operating in the constant acceleration mode. The 14.4 keV gamma radiation from a source of ^{57}Co (10 mCi) diffused into palladium was detected with a gas proportional counter and collected with a 400 channel analyzer operating in time sequence scaling mode. Typically, 10^6 counts per channel were recorded. Sample thickness was 25–30 mg/cm² (corresponding to on the order of 8–10 mg Fe/cm²). The source and drive were calibrated against a single crystal of sodium nitroprusside (National Bureau of Standards, Standard Reference Material No. 725). The quadrupole splitting for sodium nitroprusside was taken as 1.7048 ± 0.0025 mm/sec (Grant *et al.*, 1969). All isomer shifts are reported with respect to the zero position of this standard. The data were reduced by a computer program which performed a non-linear least-squares fit to the product of a series of absorption peaks having Lorentzian shapes superposed on a parabolic baseline, a result of our particular drive geometry. All of the variables (peak height, position, and half-width) were allowed to vary independently.

Although the mineral specimens did not show preferred orientation, the angle of the sample relative to the direction of γ -radiation was varied to determine if there was any resonance anisotropy due to sample preparation. None was observed.

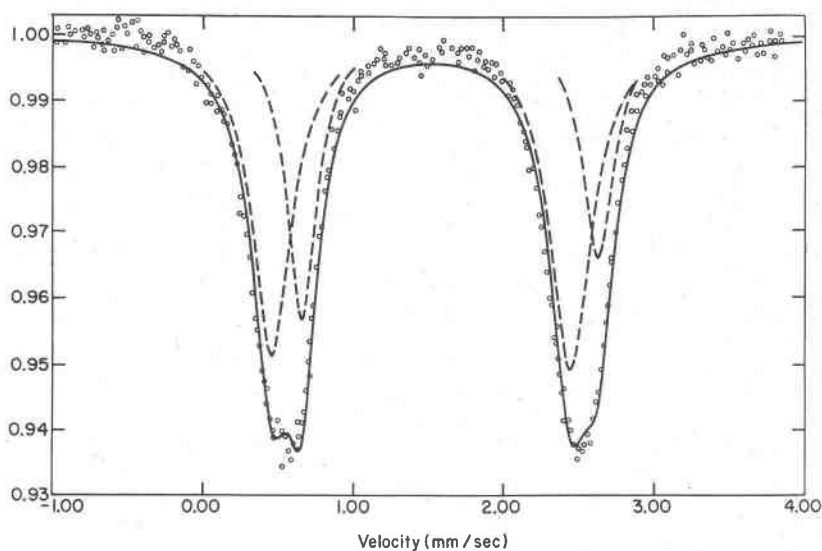
RESULTS AND DISCUSSION

The assignment of the quadrupole-split pairs is unambiguous in triplite since there is a good peak separation and a large definite difference in peak areas (see Figure 1a) in addition to the factors mentioned below. The other three minerals present a problem in assignment. If one considers peak area as a criterion for assignment (the quadrupole-split pair should have the more nearly equal areas) then peaks one and three (numbering from left to right) result from one iron ion, peaks two and four from the other. This, however, gives unusually low values for the isomer shift for half of the ferrous ions (<1.30 mm/sec), implying a rather large degree of covalency (Walker *et al.*, 1961); an effect which one would not expect to find in a phosphate mineral. The Mössbauer parameters summarized in the table are arrived at by following the assignment in triplite and show isomer shifts and quadrupole splittings characteristic of high-spin (ionic) divalent iron. As is to be expected, the isomer shifts are nearly the same for non-equivalent sites with similar coordination in a particular compound. Figures 1a and 1b illustrate the least-squares fit (solid lines) to the experimental data (circles) for triplite and triploidite, respectively. The dashed curves indicate the individual peaks.

Another point of interest is the relatively high values for the line widths observed for these minerals. The natural line width (full-width



(a)



(b)

Fig. 1: Mössbauer spectra of a) triplite b) triploidite. Velocity scale is relative to sodium nitroprusside. Solid line is a least-squares fit, dashed lines are the individual peaks, and circles indicate the normalized data.

at half-maximum—FWHM) for ^{57}Fe is approximately 0.2 mm/sec (Wertheim, 1964). (The experimental line width of our source is 0.23 mm/sec.) In the case of the hydroxy minerals triploidite and wolfeite, this can be easily explained by recalling that the two differently coordinated sites arbitrarily labeled $M(1)$ and $M(2)$ actually each represent four closely related but crystallographically unique atom positions, the broadened peaks representing sets of four unresolvable peaks. The

asymmetry of the quadrupole split peaks observed in triplodite (Figure 1b) could also be due to this effect.

A more subtle effect is observed in the fluoride minerals triplite and zwieselite. The inner set of peaks in particular are markedly broader in triplite (Figure 1a) and still remain broad in zwieselite, with a higher iron to manganese ratio. A possible rationalization of this phenomenon becomes evident when one considers an unusual aspect of the crystal structure of triplite—the splitting of the single fluorine position into two half-occupied sites at a distance of 0.62 Å to each other (Waldrop, 1970). The fluorine does not occupy a single crystallographic site with occupancy of 1.00 in triplite but partially occupies two distinct sites with average occupancy 0.50. This effect allows highly distorted six-coordination about both of the unique metal atom sites. However, if one considers the dissimilar metals which occupy these sites in the mineral (*vide supra*), one can visualize a fair amount of microscopic disorder occurring from a degree of randomization of the fluoride ion between these two partially occupied positions which is reflected in the substantial broadening of the resonance peaks. Although the structural analysis of triplite is undoubtedly correct on a macroscopic basis, a more accurate determination of the effect of the partially occupied

TABLE 1. MÖSSBAUER EFFECT PARAMETERS

(all values in mm/sec with an estimated error of ± 0.006 mm/sec)

Mineral	Site	Isomer*	Quadrupole Splitting	FWHM†	Ratio of Areas (M1/M2)
Triplite (Mn,Fe) ₂ PO ₄ F	M(1)	1.484	2.700	0.35	1.11
	M(2)	1.531	2.010	0.72	
Zwieselite (Fe,Mn) ₂ PO ₄ F	M(1)	1.500	2.622	0.40	.81
	M(2)	1.543	1.951	0.68	
Triplodite (Mn,Fe) ₂ PO ₄ OH	M(1)	1.448	2.148	0.31	.87
	M(2)	1.456	1.776	0.32	
Wolfeite (Fe,Mn) ₂ PO ₄ OH	M(1)	1.415	2.215	0.32	.93
	M(2)	1.415	1.757	0.32	

* Relative to sodium nitroprusside.

† Full-width at half-maximum.

fluorine positions on the metal atom sites seems worth undertaking. A further point of information is the complete structural determination of one of the synthetic end members of this solid solution, manganese fluorophosphate $Mn_2(PO_4)F$ (Rea and Kostiner, 1972), which places the full fluorine atom essentially between the half-occupied sites postulated for triplite with no randomization at all.

The Mössbauer effect can allow one to determine the distribution of iron atoms over crystallographically unique sites in a particular crystal structure providing that the recoil-free fraction (f) is the same for all cation sites under consideration. However, it has been shown (Sawatzky *et al.*, 1969) that a room temperature determination of occupancy factors is not necessarily accurate and that an error of 5–10 percent is to be expected. The last column in the table gives the ratio of iron atoms over the two sites ($M(1)$ and $M(2)$) in each of the minerals. Note that in the case of triploidite and wolfeite the eight metal sites are considered to be subgroups of the two distinct sites in triplite. This approximation can be justified on the basis that in both structures two groups of sites are each similar in coordination to the two different sites in triplite and that the spectra cannot be analytically resolved into any more than two sets of overlapping doublets. Because of the errors involved and the lack of any distinguishing trend, no definite conclusions regarding site preferences can be considered.

The following trends in the data can be observed. First, the isomer shifts for the fluoride minerals are greater than for the hydroxide minerals. This can be explained by noting that the cation polyhedra are made up of four oxygen atoms and two fluorine ions in the fluoride minerals and two hydroxides replacing the fluoride ions in the hydroxide minerals. Fluorine, with a higher electronegativity than oxygen, is more effective in withdrawing s -electron density from the iron nucleus, causing the higher isomer shift (Wertheim, 1964). Second, differences in quadrupole splittings are greater for the fluorides than the hydroxides, undoubtedly due to the greater effect that fluorine has on the net electric field gradient. Since a ferrous ion occupying a more distorted lattice site normally has a smaller quadrupole splitting (Ingalls, 1964), the resonance labeled $M(2)$ for triploidite and wolfeite is assigned to the trigonal bipyramidal sites with a slight but inconclusive preference of the iron atoms for this site.

ACKNOWLEDGMENTS

Thanks are due to J. Steger for developing the curve fitting program. This work was supported in part by the Advanced Research Projects Agency through the Materials Science Center, Cornell University.

REFERENCES

- FRONDEL, C. (1949) Wolfeite, xanthoxenite, and whitlockite from the Palermo Mine, New Hampshire. *Amer. Mineral.* 34, 692-705.
- GRANT, R. W., R. M. HOUSLEY, AND U. GONSER (1969) Nuclear electric field gradient and mean square displacement of the iron sites in sodium nitroprusside. *Phys. Rev.* 178, 523-530.
- HEINRICH, E. W. (1951) Mineralogy of triplite. *Amer. Mineral.* 36, 256-271.
- INGALLS, R. (1964) Electric-field gradient tensor in ferrous compounds. *Phys. Rev.* 133, A787-A795.
- PALACHE, C., H. BERMAN, AND C. FRONDEL (1944) *System of Mineralogy of Dana, 7th Ed., Vol. 2*, John Wiley and Sons, New York.
- REA, J. R., AND E. KOSTINER, (1972) The crystal structure of $Mn_2(PO_4)F$. *Acta Crystallog.* B28, (in press).
- SAWATZKY, G. A., F. VAN DER WOUDE, AND A. H. MORRISH (1969) Recoilless-fraction ratios for Fe^{57} in octahedral and tetrahedral sites of a spinel and a garnet. *Phys. Rev.* 183, 383-386.
- WALDROP, L. (1969) The crystal structure of triplite, $(Mn,Fe)_2FPO_4$. *Z. Kristallogr.* 130, 1-14.
- (1970) The crystal structure of triploidite and its relation to the structures of other minerals of the triplite and triploidite group. *Z. Kristallogr.* 131, 1-20.
- WALKER, J. C., G. K. WERTHEIM, AND V. JACCARINO (1961) Interpretation of the Fe^{57} isomer shift. *Phys. Rev. Lett.* 6, 98-101.
- WERTHEIM, G. K. (1964) *Mössbauer Effect: Principles and Applications*, Academic Press, New York.

Manuscript received, February 5, 1972; accepted for publication, April 13, 1972.