American Mineralogist, Volume 64, pages 599–603, 1979

Cation distribution in franklinite by nuclear magnetic resonance

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Abstract

The distribution of transition-metal ions between the tetrahedral and the octahedral sites in franklinite has been determined by observing the ^{55}Mn and ^{57}Fe nuclear magnetic resonance at 1.6 K, using the spin-echo method. Spectra have been interpreted by comparison with manganese ferrite spectra. From the dependence of resonance frequency on the external magnetic field, the Mn^{2+} ions were determined to be at the tetrahedral sites, while the Fe^{3+} ions are at the octahedral sites. Considering the Mn^{3+} ions to be located at the octahedral sites, the cation distribution formula is $Zn^{2+}_{0.61}Mn^{2+}_{0.39}[Mn^{3+}_{0.06}Fe^{3+}_{1.94}]O_4$, neglecting minor components.

Introduction

Minerals with the spinel structure (space group *Fd3m*) have been widely studied by many researchers. Franklinite is a familiar spinel mineral, commonly given the formula $(Zn,Mn,Fe)(Fe,Mn)_2O_4$. Most of the published works on franklinite have been related to crystallographic properties (Mason, 1947; Annersten and Hafner, 1965) and to mineralogical relationships of the individual inclusion minerals (Metsger *et al.*, 1958; Frondel and Klein, 1965). Franklinite ordinarily has a cubic spinel structure; however, when the manganese content is high, it may have tetragonal symmetry due to the Jahn-Teller effect of Mn^{3+} ions (Mason, 1947; Dunitz and Orgel, 1957). The mineral also shows ferrimagnetism similar to magnetite, Fe_3O_4. These properties depend on the quantitative distribution of the transition-metal ions Fe^{2+}, Fe^{3+}, Mn^{2+}, Mn^{3+}, and Zn^{2+} between two kinds of cation sites.

In order to understand the magnetic and the crystallographic properties of franklinite, it is important to determine the metal-ion distribution between tetrahedral (A) sites and octahedral (B) sites. We have investigated the metal ion distribution in franklinite by using ^{55}Mn and ^{57}Fe nuclear magnetic resonance (NMR). Nuclear magnetic moments of transition-metal ions in ordered magnetic materials are affected by the intrinsic local magnetic field, due to the hyperfine interaction with their unpaired *d*-electrons (Freeman and Watson, 1965). The value of the hyperfine field varies not only with the kind of atom but also with changes in its valence state.

Contents of transition-metal ions in the sites can be determined, since the following NMR spectra of ferrimagnetic spinels have already been reported: Mn^{2+} at the A site and the B site (Yasuoka, 1964 and 1966), Mn^{3+} at the B site (Kubo *et al.*, 1969) and Mn^{4+} at the B site (Kubo *et al.*, 1966); Fe^{2+} at the B site (Mizoguchi and Inoue, 1966) and Fe^{3+} at the A site and the B site (Boyd *et al.*, 1962; Abe *et al.*, 1963).

Experimental procedure

Sample

A few pieces of franklinite single crystals, from Franklin, New Jersey, were used. No information is available as to the precise occurrence of the specimen in the mine. The crystals were picked out as nearly regular octahedra from the matrix (zincite and willemite) in which they were embedded. The crystals were confirmed to be a single phase with a cubic spinel structure by means of the X-ray powder diffraction method. The lattice constant was found to be 8.466±0.004A.

The crystals were ground into fine powder with an agate mortar and were sealed in a quartz tube about 8 mm in diameter for the NMR measurements.

NMR technique

The NMR measurements were performed by the ordinary spin-echo method. The block diagram for the pulsed NMR spectrometer is shown in Figure 1. The whole apparatus is made up of three parts which are the timing, the exciter, and the receiver systems.

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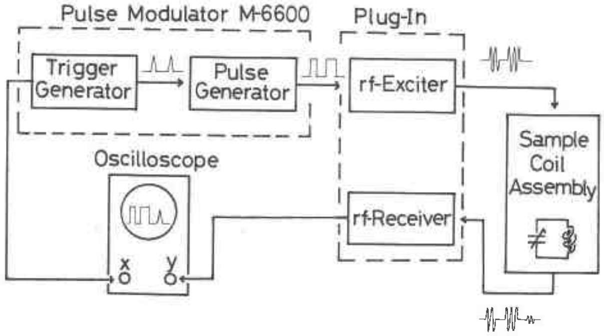

Fig. 1. Block diagram for pulsed NMR experiment.

The experiment was performed by using the Model 6600 Pulse Modulator and Receiver Models 760, 765 and 770 rf Plug-Ins made by Matec Company, Ltd. The measurement was done in the following way: first the receiving system was tuned to the reference frequency generated from a standard VHF/UHF signal generator by observing the 1 KHz-modulated wave on the oscilloscope to be at a maximum; and second the exciter system was tuned to the same frequency by adjusting the intensity of the spin-echo signal, as observed in the oscilloscope, to be at a maximum. The NMR both of ^{55}Mn and of ^{57}Fe have been investigated at liquid He, liquid N_2, and room temperatures with and without application of an external magnetic field.

Experimental results

Spin-echo spectra of the ^{55}Mn NMR in franklinite were observed in the frequency range from 300 to 600 MHz at 1.6 K in zero external magnetic field. Similarly spin-echo spectra of the ^{57}Fe NMR were obtained in the frequency range from 67 to 74 MHz under the same condition. The results are shown in Figure 2 and Figure 3.

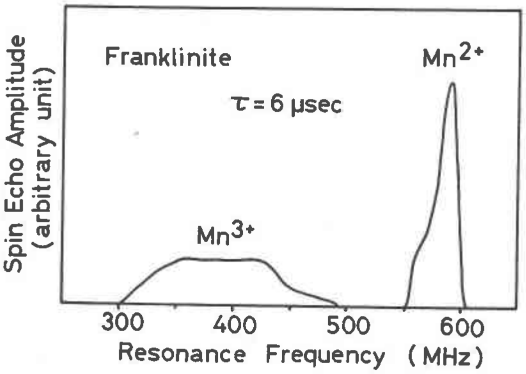

Fig. 2. Spin-echo spectrum of ^{55}Mn NMR of powdered franklinite specimen at 1.6 K under zero external magnetic field, where τ denotes time interval between 1st and 2nd pulses.

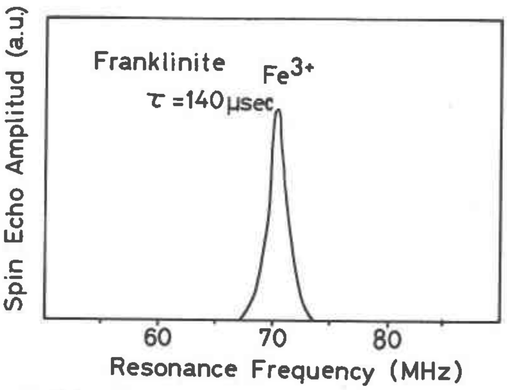

Fig. 3. Spin-echo spectrum of ^{57}Fe NMR of powdered franklinite specimen at 1.6 K under zero external magnetic field.

In Figure 4 and Figure 5 the spin-echo spectra of the ^{55}Mn and the ^{57}Fe NMR in manganese ferrite $MnFe_2O_4$ (Kubo, 1970) are shown for comparison. From the previous work, the strong signal between 570 and 590 MHz in Figure 4 is assigned to the ^{55}Mn NMR associated with the Mn^{2+} ions at the A sites, and the broad signal between 300 and 500 MHz to the Mn^{3+} ions at the B sites. In Figure 5 the double peaks of the NMR signal between 67 and 73 MHz are due to the ^{57}Fe NMR associated with the Fe^{3+} ions. The signal of the higher frequency peak corresponds to the ^{57}Fe NMR associated with the Fe^{3+} ions in the B-sites (Fe^{3+}_B) and the other one corresponds to those in the A-sites (Fe^{3+}_A). Note that the relative intensity ratio of Fe^{3+}_A to Fe^{3+}_B in Figure 5 is about 1:8, as expected from the ion distribution formula of manganese ferrite $Mn^{2+}_{0.8}Fe^{3+}_{0.2}[Mn^{3+}_{0.2}Fe^{2+}_{0.2}Fe^{3+}_{1.6}]O_4$ (Harrison *et al.*, 1957; Krupička and Závěta, 1959). The weak spectrum around 60 MHz is due to the ^{57}Fe NMR of the Fe^{2+} ions at the B sites.

Comparing the NMR spectra in franklinite with those of manganese ferrite, the following is deduced.

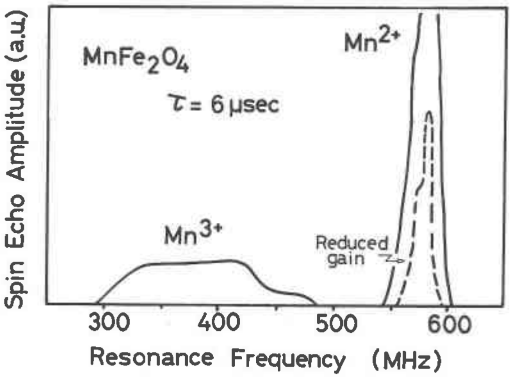

Fig. 4. Spin-echo spectrum of ^{55}Mn NMR of powdered manganese ferrite $MnFe_2O_4$ specimen at 1.6 K under zero external magnetic field.

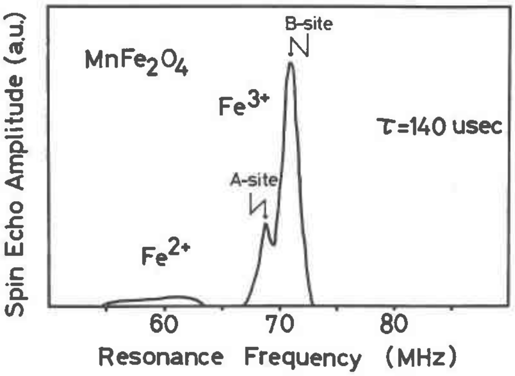

Fig. 5. Spin-echo spectrum of ^{57}Fe NMR of powdered manganese ferrite MnFe$_2$O$_4$ specimen at 1.6 K under zero external magnetic field. Double peak corresponds to ^{57}Fe NMR of Fe^{3+}ions at A and B sites as indicated. Weak spectrum around 60 MHz is due to ^{57}Fe NMR of Fe^{2+} ions at B sites.

Firstly in Figure 2 the strong signal between 550 and 610 MHz is due to the ^{55}Mn NMR associated with the Mn^{2+} ions, and the broad signal between 300 and 500 MHz is due to the Mn^{3+} ions at the B sites. The width of this signal is due to Jahn-Teller distortion (Kubo *et al.,* 1969). Secondly in Figure 3 the NMR signal of symmetrical shape between 67 and 74 MHz originates from the ^{57}Fe NMR associated with the Fe^{3+} ions. Careful detection was performed between 50 and 65 MHz at 1.6 K, but no ^{57}Fe NMR associated with the Fe^{2+} ions was observed. Although careful measurement is necessary to observe the NMR signal of the Fe^{2+} ions ($3d^6$, ^5D) because of shortness of the spin-echo-decay time and broadening of the resonance spectrum due to the anisotropic component of the hyperfine field (Mizoguchi and Inoue, 1966), it is evident that scarcely any Fe^{2+} is present in the franklinite examined.

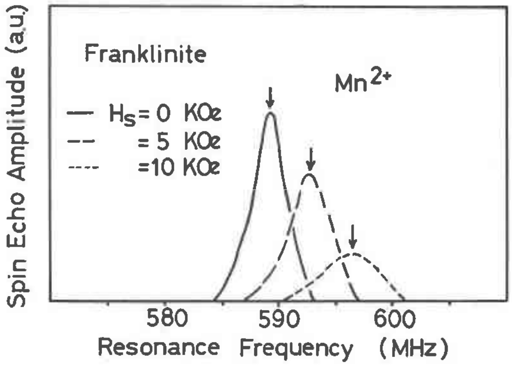

Fig. 6. External magnetic field dependence of ^{55}Mn NMR of Mn^{2+} ions in franklinite at 1.6 K. Increasing of resonance frequency means that hyperfine field of Mn^{2+} ion in franklinite is parallel to external magnetic field.

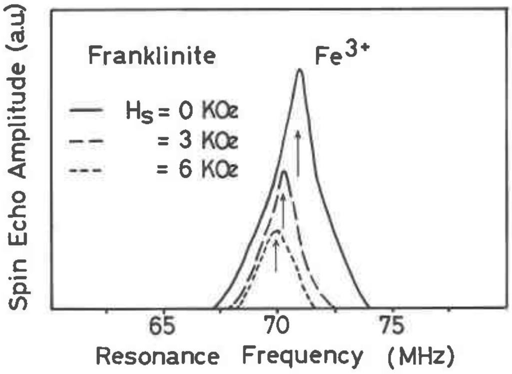

Fig. 7. External magnetic field dependence of ^{57}Fe NMR of Fe^{3+} ions in franklinite at 1.6 K. Decreasing resonance frequency means that hyperfine field of Fe^{3+} ion in franklinite is antiparallel to external magnetic field.

In order to determine the site occupancy of the Mn^{2+} ions, the spin-echo spectrum of the ^{55}Mn NMR in franklinite was investigated at 1.6 K under the application of an external magnetic field. The result is shown in Figure 6. By increasing the external magnetic field, the signal shifts toward higher frequency. In a similar way the spin-echo spectrum of the ^{57}Fe NMR was observed under the same condition. The external field dependence of this signal is shown in Figure 7. When the external magnetic field is increased, the signal shifts to lower frequency while maintaining a symmetrical line shape. In order to interpret these results for the external field dependence of the resonance frequency, one must take into account the following point. If the hyperfine fields of the transition-metal ions are opposite to the direction of the local magnetic moment, the relations between each sublattice moment and each hyperfine field in a

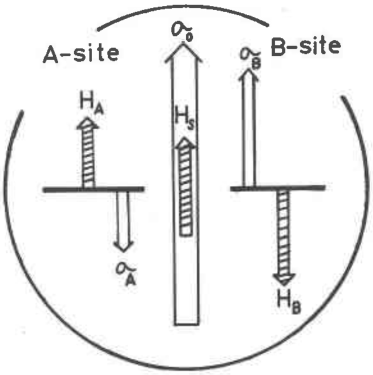

Fig. 8. Mutual direction between each sublattice moment (σ_A, σ_B) and each hyperfine field (H_A, H_B) in ferrimagnetic spinel under application of saturating external magnetic field (H_S) when B-sublattice moment dominates. Resultant moment (σ_0) is parallel to external magnetic field.

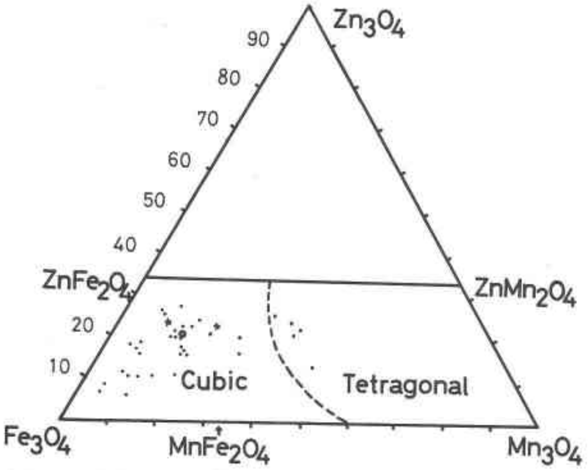

Fig. 9. Equilibrium diagram for Zn–Mn–Fe spinels (Mason, 1947) and composition of franklinite. Open circle–present analysis; solid circles–Frondel and Klein, 1965; stars–Palache, 1935.

ferrimagnetic spinel can be shown as in Figure 8, under the application of the saturating external magnetic field when the B-sublattice moment dominates (Smit and Wijin, 1959; Freeman and Watson, 1965). For the case of both the Mn^{2+} and Fe^{3+} ions with five $3d$-electrons (S-state ion), the main part of the hyperfine field is due to the Fermi contact interaction and in the direction opposite to the local moment. Accordingly, in the presence of an external field the resonance frequency decreases for an S-state ion (Fe^{3+} and Mn^{2+}) having a magnetic moment parallel to the direction of the external field and increases for an S-state ion having a magnetic moment antiparallel.

Therefore, the experimental result shown in Figure 6 leads to the conclusion that the Mn^{2+} ions are located at the A sites but not at the B sites. Similarly the experimental result shown in Figure 7 leads to the conclusion that the Fe^{3+} ions are located at the B sites only.

The NMR measurements were also tried at higher temperatures. At 77 K only the NMR signal due to the Mn^{2+} ions was observed, and the signals associated the Mn^{3+}, Fe^{2+}, and Fe^{3+} ions could not be observed. At room temperature, no NMR signal was observed.

Discussion

From chemical analysis using the EDTA titration method, the average composition of the crystals was determined to be ZnO 21.00, MnO 13.49, and Fe_2O_3 65.56 percent, disregarding the elements in minor concentrations. Accordingly one obtains the following chemical formula, without minor elements, for the franklinite crystals:

$$Zn_{0.61}Mn_{0.45}Fe_{1.94}O_4 \qquad (1)$$

Analyses of franklinite have been given by Palache (1935), Mason (1947), and Frondel and Klein (1965). The available analytical data are plotted in Figure 9, where the composition of the present sample is also shown. The present specimen evidently does not differ very much from ordinary franklinite in the atomic ratios of Fe, Mn, and Zn.

It is well known that Zn^{2+} ions have a marked preference for the A sites in spinel, as in zinc ferrite $ZnFe_2O_4$ (Verwey and Heilmann, 1947). Combining this with the above NMR results, the following formula is obtained:

$$Zn^{2+}_{0.61}Mn^{2+}_{0.39}[Mn^{3+}_{0.06}Fe^{3+}_{1.94}]O_4 \qquad (2)$$

The occurrence of Mn^{3+} at the B site is consistent with previous results for $MnFe_2O_4$ (Harrison *et al.*, 1957; Krupička and Závěta, 1959; Miller, 1960; Červinka, 1965), hausmannite, Mn_3O_4 (Finch *et al.*, 1957), and $CuMn_2O_4$ (Buhl, 1969). The high octahedral site preference energy of Mn^{3+} compared to Mn^{2+}, Fe^{2+}, and Fe^{3+} (Dunitz and Orgel, 1957; McClure, 1957) must be at least partially responsible for this behavior.

No Fe^{2+} ions appear to be present in the franklinite studied. Although the NMR detectability for this ion is poor, its absence is supported by the absence of Mn^{3+} or Fe^{3+} at the A site, which would be required to maintain charge balance. The difference between franklinite and $MnFe_2O_4$ in this respect may be due to the high content of Zn^{2+} in franklinite.

The formula (2) should be considered an average, since both NMR measurements and the chemical analysis were performed on a specimen which was powdered from several franklinite crystals. We must also bear in mind that other elements are present in minor concentration: small and variable amounts of Mg and Al, to as much as 0.03 atoms per formula unit, were detected by electron microprobe analysis.

Acknowledgments

The authors thank Professor A. Hirai for his encouragement and helpful discussions, Dr. N. Yamamoto for chemical analysis and valuable discussions, Mr. S. Hiraga and Mr. A. Minami for EPMA measurement, and Dr. J. M. Goodwin for careful reading of the manuscript.

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Manuscript received, July 11, 1978;
accepted for publication, January 10, 1979.