Mössbauer spectra, magnetic and electrical properties of laihunite, a mixed valence iron olivine mineral

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Abstract

Laihunite is an olivine mineral with ideal composition $Fe^{2+}Fe_2^{3+}(SiO_4)_2$. Alternate M1 sites are occupied by Fe^{2+} whereas Fe^{3+} occupies the M2 sites. Small (~ 1 mm) crystals from Laihe, N.E. China exhibit thermally-activated electrical conduction in the range 290–500 K with an activation energy of 0.53 eV. Resistivity at 290 K is 2.2×10^5 Ωm. Mössbauer data show that ferric iron begins to order magnetically below 160 ± 5 K, but that hyperfine splitting for ferrous iron only appears below 100 K. An antiferromagnetic structure is proposed which is consistent both with the crystal structure and with the magnetization curves that indicate antiferromagnetic interactions. Magnetization measurements also show that magnetite inclusions account for less than 0.5 wt.% of the sample. Analysis of the 4.2 K Mössbauer spectrum suggests that there is a distortion of the structure at low temperatures which leads to inequivalent M1 and M2 sites, each with relative populations of 2:1. In addition, $5 \pm 2\%$ of the total iron is identified as Fe^{2+} on M2 sites. This supports evidence from X-ray diffraction which indicated that roughly 10% of the crystal is composed of twin boundary regions with a concentration of divalent ions approaching that of fayalite.

Introduction

Laihunite is a new iron nesosilicate mineral, whose discovery in a metamorphic iron deposit at Laihe village in Liaoning Province, N.E. China was reported in 1976 (Laihunite Research Group 1976). It was originally found to occur as a minor constituent (1–4%) of a quartz-hypersthene granulite. Several other occurrences were reported subsequently, and the mineral is thought to have been derived by oxidation of fayalite (Kitamura et al., 1984). Laihunite is frequently associated with magnetite. Kitamura et al. used electron microscopy to show that some of the magnetite may be present as fine-grained inclusions in the laihunite grains, which typically range in size from 0.3–0.7 mm. Like magnetite, laihunite is black in color, with a submetallic luster.

The first complete mineralogical study established the chemical composition as $Fe_{1.00}^{3+}Fe_{0.58}^{2+}Mg_{0.03}Si_{0.96}O_4$ and the mineral was assigned to the monoclinic space group $P2_1/c$ with unit cell parameters $a = 5.813$, $b = 4.812$, $c = 10.211$Å and $\beta = 90.87°$ (Laihunite research group 1982). However, detailed structural analysis has revealed that laihunite crystals are not perfectly ordered, but consist of antiphase domain regions alternating along the **a**-axis (Fu et al., 1982). As a result of this twinning, the crystallites appear to have orthorhombic symmetry. **a**-axis superlattice structures have also been identified (Shen et al., 1982).

The ideal structure of laihunite within a domain is relat-

ed to that of olivine in the way indicated on Figure 1. All M2 positions are occupied by Fe^{3+} whereas M1 positions are alternately vacant and occupied by Fe^{2+}. Shinno (1981) and Schaefer (1983) have recently described natural ferric olivines that contain lesser amounts of ferric iron, also tentatively assigned by Shinno to M2 sites. The ideal formula of laihunite is $Fe^{2+}Fe_2^{3+}(SiO_4)_2$, and Fu et al. (1982) suggested that it might be regarded as the end-member of a sequence of iron olivine minerals, fayalite–tallaskite–ferrifayalite–laihunite, with general formula $Fe_{4-3x}^{2+}Fe_{2x}^{3+}\square_x(SiO_4)_2$ where vacancies appear progressively in M1 positions as the ferric/ferrous ratio increases from 0 for fayalite to 2 for laihunite. The relations between M1 and M2 octahedra within the domains are illustrated in Figure 2. Some relevant points are:

(1) Fe^{3+} octahedra are linked by shared vertices in puckered planes normal to **c**. The Fe–O–Fe bond angle is 129° and the Fe^{3+}–Fe^{3+} distance is 3.72Å when O_3 is the shared vertex, but the bond angle is 136° and the distance is 3.89Å when O_4 is the shared vertex.

(2) Fe^{2+} octahedra are not directly linked to each other because half the M1 sites are vacant.

(3) Adjacent Fe^{2+} and Fe^{3+} octahedra either share an edge O_2–O_4 or a vertex O_1. Fe–Fe distances are, respectively, 3.18Å and 3.66Å and the bond angles are 99° for O_2, 93° for O_4 and 124° for O_1.

The real structure of laihunite is characterized by a high degree of twinning of the monoclinic domains. Boundary regions with a distorted lattice and a concentration of divalent ions approaching that of fayalite were reported to constitute 14% of the whole crystal (Fu et al., 1982).
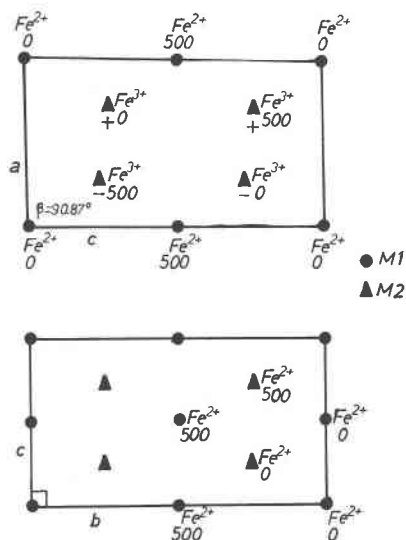
Fig. 1. Comparison of the octahedral cation positions in laihunite above and fayalite below.

Fig. 2. Part of the ideal laihunite structure showing some of the connections between the iron–oxygen octahedra.

An earlier Mössbauer study of laihunite (Kan et al., 1980) in the temperature range 80–295 K showed evidence for an unusual magnetic order–disorder transition. Spectra at lower temperatures of several ferrifayalites with differing amounts of ferric iron have also been reported (Schaefer, 1983b). In the present paper we offer a complete Mössbauer analysis, together with an account of the magnetic and electrical properties of laihunite which help to establish its status as a new, mixed-valence iron silicate.

Experimental results

Approximately 150 mg of pure laihunite crystals from Laihe were hand picked under a microscope for the experimental investigations reported here. The material is similar to that characterized by the Laihunite Research Group (1982) and Fu et al. (1982).

Mössbauer spectroscopy

Mössbauer spectra were recorded on a conventional constant-acceleration spectrometer using a source of ^{57}Co in rhodium. Isomer shifts are quoted relative to an iron metal absorber. Absorbers were made from crystallites of laihunite ground to a fine powder and mixed with finely ground sugar. An absorber with 2 mg of iron per cm^2 was used for the room-temperature spectrum of Figure 3a, but a thicker absorber (4 mg/cm^2) was used for some of the lower temperatures. Also included for comparison in Figure 3b is the spectrum of an olivine from San Carlos Co., Arizona, containing 6 wt.% FeO, but almost no Fe^{3+}. A reasonable least-squares fit to the room-temperature laihunite spectrum is obtained with two quadrupole doublets, one ferrous and the other ferric, attributed to M1 and M2 sites respectively on the basis of the crystal structure refinement of Fu et al. (1982). (The average Fe–O distance is 0.14Å greater for M1 sites than for M2 sites). Fit parame-
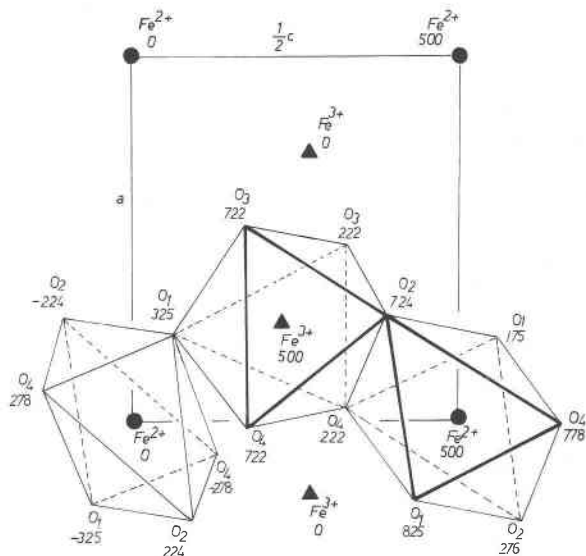
ters are included in Table 1 with estimated errors. The intensity ratio of the two doublets is in reasonable agreement with the chemical formula. Linewidths for both patterns are greater than the instrumental resolution, $\Gamma_o = 0.25$ mm/s, but they are not exceptionally broad for an end-member silicate mineral (Coey, 1984). There is no sign of identifiable magnetite absorption nor of any separate ferrous absorption from the boundary regions. However it should be remarked that the absorption due to a few percent of superparamagnetic Fe_3O_4 might be hidden in the
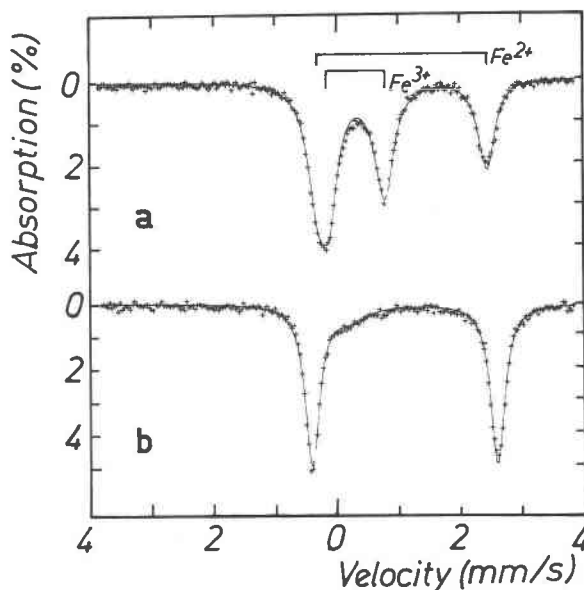

Fig. 3. Room temperature Mössbauer spectra (a) of laihunite and (b) of ferrous olivine.

Table 1. Least-squares fit parameters for laihunite Mössbauer spectra

Temperature (K)	Site		δ (mm/s)	Γ (mm/s)	Δ (mm/s)	B_{hf} (T)	I (%)
290	Fe^{2+}	M1	1.13(1)	0.33(2)	2.75(2)		41(3)
	Fe^{3+}	M2	0.39(1)	0.37(2)	0.91(2)		59(3)
4.2	A Fe^{3+}	$M2_1$	0.49(3)	0.64(5)	0.52(6)	51.8(4)	42(3)
	B Fe^{3+}	$M2_2$	0.50(3)	0.78(5)	0.03(5)	49.7(4)	19(3)
	C Fe^{2+}	$M1_1$	1.32(3)	1.22(10)	2.80(6)	24.0(10)	22(2)
	D Fe^{2+}	$M1_2$	1.32(4)	0.81(10)	3.10(10)	28.1(10)	13(2)
	E Fe^{2+}	M2	1.30(5)	0.79(10)	3.03(10)	12.1(15)	5(2)

δ : Isomer shift relative to iron metal

Γ : Linewidth-full width at half maximum

Δ : Quadrupole interacton

B_{hf} : Magnetic hyperfine field

I : Relative intensity

η : Asymmetry parameter for C, D and E is > 0.1

Estimated errors are given in parentheses.

central part of the spectrum, and that even in fayalite (Schaefer, 1983a) the Mössbauer spectra of M1 and M2 ferrous iron overlap at room temperature so that only a single quadrupole doublet with parameters $\delta = 1.16$ mm/s, $\Delta = 2.80$ mm/s and $\Gamma \simeq 0.37$ mm/s is observed.

Some of the low-temperature Mössbauer spectra are shown in Figure 4. The temperature-dependence of the laihunite spectrum is quite unusual. First the ferric paramagnetic doublet decreases in intensity between 200 K and 100 K to the profit of a magnetically-split ferric hyperfine pattern, but the ferrous doublet only begins to split magnetically below about 100 K. At 4.2 K, there is a complex hyperfine spectrum which is the superposition of several magnetic patterns, both ferric and ferrous. Evidence to two unusual ferric patterns is clearly seen in the asymmetric structure of the high-velocity line near 10 mm/s. Considerable effort was devoted to fitting the 4.2 K spectrum using the least squares Mössbauer program of Teillet and Varret (unpublished) which allows up to ten independent hyperfine patterns to be adjusted, including full matrix diagonalization when appropriate for Fe^{2+} and variable linewidths within each pattern. More than one or two ferrous patterns are definitely required, and our best fit of the whole spectrum is obtained with two ferric and three ferrous patterns whose hyperfine parameters are listed in Table 1. Their interpretation is given in the discussion section. There is also evidence from the misfit between experimental and calculated spectra perceptible in the central region of Figure 4 that a small amount of paramagnetic Fe^{2+} representing 1-2% of the total cations may be present as an impurity phase.

A thermal scan of the Mössbauer count rate at zero velocity is shown in Figure 5. The temperature where ferric hyperfine splitting begins to appear is identified from these data as 160 ± 5 K, whereas that for ferrous hyperfine splitting is approximately 100 K.

Magnetic properties

The magnetization curves for powder samples in fields of 0–1.7 T have been measured at room temperature and 77 K using a vibrating-sample magnetometer. The two curves are quite similar, each showing a readily-saturated ferromagnetic or ferrimagnetic component with a spontaneous magnetization of 0.4 $JT^{-1}kg^{-1}$, followed by a high field slope of 0.3 $JT^{-2}kg^{-1}$. The readily saturated component is attributed to a tiny proportion (~ 0.4 wt.%) of magnetite inclusions. The small high-field susceptibility with little temperature dependence points to the presence of strong antiferromagnetic interactions, and indicates that the magnetic order manifest in the low-temperature Mössbauer data is essentially antiferromagnetic. Magnetization measurements are a particularly sensitive way of detecting the presence of small quantities of magnetite impurity in
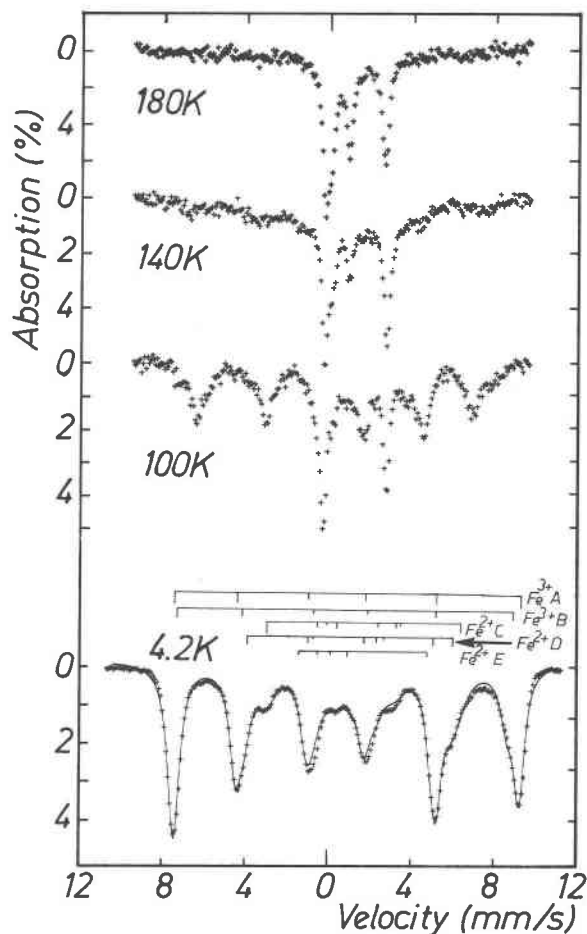

Fig. 4. Low temperature Mössbauer spectra of laihunite. Temperatures are shown in Kelvin.
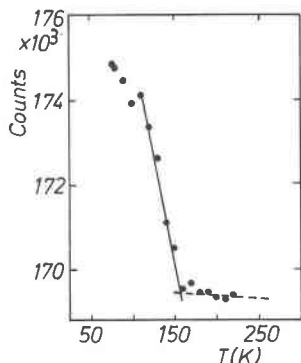
Fig. 5. Thermal scan of the Mössbauer count in 120 seconds at zero velocity.

silicate minerals, since Fe_3O_4, even in the form of ultra-fine inclusions which behave superparamagnetically, will exhibit a magnetization close to its saturation value of 100 $JT^{-1}kg^{-1}$ in a field of 1 Tesla. The present laihunite sample, unlike those of Kitamura et al. (1984), contains an insignificant amount of magnetite.

Electrical conductivity

The electrical conductivity of a single laihunite crystallite was measured in the range 300–500 K using the two contact method. The four contact method is usually preferable, but it was impracticable in the present case because of the small size of the samples, ~0.05 mm³. Several crystallites of laihunite and ilvaite were set in a resin disc 2 cm in diameter and initially 1.5 mm thick. It was polished down first on one side, then on the other to leave a wafer 0.2 mm thick with flat crystallite surfaces exposed on both sides. Contacts were then applied using silver paint. Ilvaite grains were included as a check on the method since the conductivity of another sample of this mineral had recently been measured using the four contact method (Coey et al., 1984). The measured values at room temperature were found to agree within a factor of 2. The cross sectional area of the laihunite was 0.14 mm², and its resistivity at room temperature was 2.2×10^5 Ωm. The temperature dependence of the resistivity up to 500 K was measured in a vaccum oven, using a Keithley Model 480 picoammeter. Results are shown in Figure 6, where it may be seen that the resistivity follows the activation law $\rho = \rho_o \exp(E_a/kT)$ with $E_a = 0.53$ eV. The resistivity, ρ, varies by four orders of magnitude between 300 K and 500 K. This behavior must be intrinsic to laihunite rather than a consequence of possible magnetite inclusions in the crystallites because the resistivity of magnetite itself displays a quite different temperature dependence (Goodenough 1980).

Discussion

The most conducting silicate minerals are those which contain large amounts of iron, with Fe^{2+} and Fe^{3+} cations in comparable quantities on adjacent and contiguous lattice sites (Parkhomenko, 1982). The resistivity of laihunite at room temperature and its activation energy above room temperature (2.2×10^5 Ωm; 0.53 eV), may be compared to values which have been reported for other conducting mixed valence iron silicates: ilvaite (3.3×10^3 Ωm; 0.36 or 0.67 eV, Coey et al., 1984); cronstedtite (3×10^2 Ωm; 0.25 eV. Coey et al., 1982). Like laihunite, the ferrous and feric sites in ilvaite are inequivalent at room temperature (Takéuchi et al., 1983), whereas those in the octahedral sheet of cronstedtite are crystallographically equivalent. Activated conductivity is plausibly explained by localized electron hopping between adjacent ferrous and ferric sites, some of which leads to long-range charge transport. The sites involved are likely to be M1 and M2 octahedra which share a common edge or corner, as these form continuous chains throughout the structure. The conductivity of laihunite is smaller than that of the other examples cited, probably because the dimensionality of the edge-sharing units is lower (groups of three in laihunite, double chains in ilvaite, sheets in cronstedtite). On the other hand, its conductivity is somewhat larger than that of fayalite, which normally contains little ferric iron (Parkomenko 1982). In any case, the fact that laihunite is a relatively good electrical conductor confirms that Fe^{2+} and Fe^{3+} are distributed throughout the mineral on an atomic scale, and rules out the possibility that it is a mixture of a purely ferrous olivine with an unknown ferric phase.

The unusual onset of magnetic hyperfine splitting in laihunite, ferric splitting first and then ferrous at a much lower temperature, cannot be interpreted on a two-phase mixture model in view of the conductivity data and the crystal structure analysis. However, there is another explanation which is quite consistent with the laihunite structure described in the introduction. The Fe^{3+}–O–Fe^{3+} superexchange between M2 sites in the puckered planes normal to **c** is likely to be a strongly antiferromagnetic interaction. If successive planes have the same magnetic structure, as indicated in Figure 1a by the + and − symbols, representing spin up and spin down iron, then each Fe^{2+} ion on M1 sites has 6 Fe^{3+} neighbors, two at 3.18Å and four at 3.66Å. Each pair consists of two ions on opposite sublattices so that the net exchange coupling of Fe^{2+} with Fe^{3+} is zero. Successive planes of Fe^{3+} ions are therefore decoupled from each other. Furthermore, there are no Fe^{2+}–O–Fe^{2+} interactions because of the ordered vacancies on M2 sites.

Our preliminary powder neutron diffraction data, obtained on the present sample at the Institut Laue Langevin
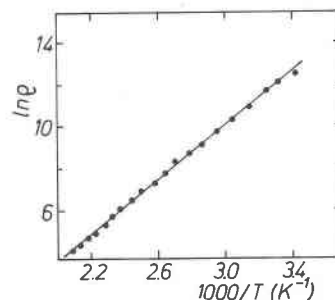

Fig. 6. Electrical resistivity of laihunite above room temperature.

in Grenoble, support the picture of antiferromagnetic ordering, since a broad and purely magnetic 010 reflection appears at 80 K. The breadth of the peak, and the extended range of temperature for the onset of Fe^{3+} hyperfine splitting may reflect the two-dimensional character of the decoupled planes of ferric ions on M2 sites.

Referring to the fitted spectrum of Figure 4 and the parameters in Table 1, it may be seen that the five subspectra fall into three groups—a pair of ferric patterns A and B with hyperfine fields of 51.8 and 49.7 T, a pair of ferrous patterns C and D with hyperfine fields of 24.0 and 28.1 T and a third ferrous pattern E with a hyperfine field of 12.1 T. But the ideal laihunite structure, determined at room temperature, contains only two inequivalent sites M1 and M2. Some possible explanations for the complexity of the 4.2 K spectrum are (1) incomplete cation order of Fe^{2+} on M1 and Fe^{3+} on M2; (2) inequivalency of M1 and M2 sites or their occupancy by ferric and ferrous iron in the ideal laihunite domains and in the twin boundary regions; (3) distortion of the crystal structure at low temperatures which splits both the M1 sites and the M2 sites into two inequivalent groups.

Neglecting for the moment pattern E which represents only $5\pm2\%$ of the total absorption, and noting that the main ferric and ferrous patterns each have an intensity ratio A:B or C:D or approximately 2:1, we consider these possibilities in turn.

If incomplete cation order were to blame, a large proportion of each type of cation would have to be on the "wrong" site (i.e., Fe^{3+} on M1, Fe^{2+} on M2). There is no evidence of this, either from the average Fe–O distances or in the room-temperature Mössbauer spectrum. Furthermore, a spectrum of fayalite at 9 K published by Kundig et al. (1967) shows that the hyperfine fields at M1 and M2 sites are quite different (32.3 and 12.0 T) whereas those of patterns C and D are rather similar.

If we associate the main ferric and ferrous patterns A and C with domains having the ideal laihunite structure, then patterns B and D might be ascribed to the boundary regions mentioned in the introduction. The difficulty with this interpretation is that the proportion of boundary regions would be implausibly large—one-third of the whole sample. And again there is no indication in the room-temperature spectrum of distinct 2+ or 3+ subspectra.

A low temperature distortion of the laihunite structure which alters the symmetry of the unit cell is the most likely explanation. It must split both M1 and M2 sites into two sets, $M1_1$ and $M1_2$, and $M2_1$ and $M2_2$, with a 2:1 ratio in each case. This idea is also supported by the preliminary neutron diffraction data which shows extra reflections appearing at 4.2 K, notably a strong peak at 9.1Å, which cannot be indexed on the monoclinic unit cell, or on any simple multiple of it.

Pattern E, which has a relative intensity of $5\pm2\%$, may be associated with Fe^{2+} on M2 sites, whether as a result of cation disorder or due to the twin boundary regions which are believed to have a composition approaching that of fayalite (Fu et al., 1982). In the latter case, these boundary regions would constitute approximately 10% of the whole crystal.

In summary, the Mössbauer, magnetic and electrical measurements on laihunite confirm that this mineral is essentially a uniform, mixed valence iron silicate with characteristic physical properties. Questions now posed are: (1) How widespread is the substitution of 3 Fe^{2+} by 2 Fe^{3+} and a vacancy in other iron olivines? and (2) Do minerals exist which form a continuous suite between fayalite and laihunite? (See also Fu et al., 1982; Schaefer, 1983b)

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