Mössbauer spectroscopy of grandidierite, $(Mg,Fe)Al_3BSiO_9$

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Abstract

The room-temperature spectrum of grandidierite is characterized by a doublet with $\Delta = 1.70$ mm sec^{-1} and $\delta = 1.10$ mm sec^{-1} (relative to metallic iron) caused by Fe^{2+} in the five-coordinated position. The quadrupole splitting decreases with increasing $Fe^{2+}/(Fe^{2+} + Mg)$ from 1.724 mm sec^{-1} at $Fe/(Fe+Mg) = 0.037$ to 1.681 mm sec^{-1} at $Fe/(Fe+Mg) = 0.288$. The temperature dependence of the isomer shift indicates a Debye temperature of 300 ± 50 K for divalent iron in this position.

Introduction

The rare borosilicate grandidierite is structurally closely related to andalusite (Stephenson and Moore 1968) and is the only silicate in which significant amounts of ferrous iron are reported to occur exclusively in fivefold coordination. The form of the coordination polyhedron around the (Mg,Fe) site is somewhere between a trigonal bipyramid and a tetragonal pyramid but can best be described as a distorted trigonal bipyramid. A number of other silicates contain ferrous iron partly in sites that may be considered as an effective five-coordination or, alternatively, as a $5 + 1$ coordination, *i.e.* a strongly deformed octahedron. Examples are rhodonite ($M4$ position, Peacor and Niizeki 1963, Dickson 1975), pyroxmangite ($M6$ position, Ohashi and Finger 1975) and pyroxferroite ($M6$ position, Burnham 1971). When the sixth oxygen atom is disregarded, polyhedra are obtained that can be described as distorted tetragonal pyramids. The five-coordinated B site in vesuvianite (Rucklidge *et al.,* 1975) is exceptional because ferrous iron (Manning and Tricker 1975) is surrounded by four oxygen atoms in a quasi-planar arrangement, with a fifth oxygen situated at nearly the same distance from the iron atom but outside the plane defined by the four oxygens. The polyhedron can thus be described as a regular tetragonal pyramid with the cation site situated practically in the base.

The Mössbauer parameters of Fe^{2+}, coordinated by oxygen, in square-planar, tetrahedral, octahedral, and cubic symmetries have been reported by many authors (see, for example, Bancroft 1973). However,

little information is available for fivefold coordinated Fe^{2+}. Because the grandidierite structure appears to have Fe^{2+} in only one site, its Mössbauer spectrum should be amenable to direct interpretation and thus provide data that are helpful for the assignment of peaks in the Mössbauer spectra of more complex silicates (*cf.* Dickson 1975, Manning and Tricker 1975). This paper, therefore, describes the spectra of several grandidierites.

Experimental

The sources of the natural grandidierite specimens and their chemical composition are given in Table 1. The material was crushed, separated by a magnetic separator and carefully handpicked. The concentrates obtained were over 99 percent pure (for possible contaminants, see Table 1). Microprobe analyses were made by K. Abraham, Ruhr University Bochum, and D. Ackermand, Kiel University. Since boron enters the structure of grandidierite in stoichiometric amounts (McKie 1965, Stephenson and Moore 1968), a boron value of 1.0 per 9 oxygens was assumed. Total iron was calculated as ferrous iron. No grain-to-grain variations or chemical zoning was observed. Lattice constants of the phases studied are reported by Olesch and Seifert (1976).

The Mössbauer spectra were taken on an Elscint spectrometer operated in the constant acceleration mode, using a ^{57}Co source in rhodium matrix with 50 mCi nominal activity. Duplicate spectra were accumulated in each half of a 1024 channel multichannel analyzer. The velocity increment per channel

Table 1. Sources and chemical composition of grandidierites

No. Source	1 Vohiboly	2 Sakatelo	3 Nampoana	4 Rhodesia
Analyst	Ackermand	Scoon in McKie 1965	Ackermand	Abraham
SiO_2	19.41	20.39	19.93	19.97
TiO_2	n.f.	0.13	0.01	n.d.
Al_2O_3	51.10	52.12	50.68	50.75
B_2O_3	n.d.	11.57	n.d.	n.d.
Fe_2O_3	n.d.	0.80	n.d.	n.d.
FeO	0.89*	2.87	4.27*	6.93*
MnO	0.01	0.04	0.04	0.08
MgO	13.02	12.04	11.16	9.63
Na_2O	n.d.	0.04	n.f.	n.d.
K_2O	n.d.	0.09	0.02	n.d.
$\dfrac{Fe^{2+**}}{Fe^{2+}+Mg}$	0.037	0.118	0.177	0.288

* Total iron
** molecular ratio

n.d. = not determined, n.f. = not found

Additional data on the source of the specimens:

1. Material kindly made available by J. Fabries, sample 163-58 of Muséum National d'Histoire Naturelle, Paris. Vohiboly, Madagascar. About 0.5 percent contamination by magnesian chlorite.
2. Material kindly made available by D. McKie. Identical to the specimen described in McKie (1965) and to that used by Stephenson and Moore (1968) in the crystal structure determination. Sakatelo, Madagascar.
3. Supplied by J.P. Fuller, British Museum Natural History, specimen BM 1962.88. From Nampoana quarry, E of Ampamatoa, N of Fort Dauphin, Madagascar, associated with phlogopite. Sample contaminated by a trace (<0.5%) of phlogopite.
4. From a grandidierite-magnetite-hercynite-corundum-apatite-tourmaline rock donated by W. Schreyer. Exact provenence unknown.

was about 0.02 mm sec^{-1}, and counting times necessary to accumulate from 2 to 14 × 10⁵ counts per channel were employed. The reported parameters represent the average of the left- and right-hand sides that were fitted independently. Velocity calibration was made against the spectrum of Fe foil (Violet and Pipkorn 1971), and isomer shifts are reported relative to metallic iron.

The grandidierite samples were ground to a fine powder. For experiments at room temperature and liquid nitrogen temperature the material was baked into a pellet with transoptical powder. For higher absorber temperatures the material was packed between thin aluminium foils. Sample thicknesses generally ranged from 1 to 4 mg Fe/cm² (Table 2). The spectra were fitted to Lorentzian shaped peaks, and the sum of the normalized squares of the difference between each channel count and the value of the sum of Lorentzians at this channel (χ^2) was minimized.

Results

The different grandidierite specimens gave very similar Mössbauer absorption spectra, characterized by an intense doublet (called A in the following) and a weak doublet (B). Figure 1 shows the spectrum of the material from the same locality and batch that served in the crystal-structure determination by Stephenson and Moore (1968). The spectra could be fitted by four Lorentzian peaks (12 peak variables, one background variable). In some cases constraints had to be used for the weak doublet (cf. Table 2). In sample 1 only one doublet (A) was encountered. Peak intensities, half-widths, quadrupole splittings and isomer shifts are reported in Table 2. It should be pointed out that the B doublet only accounts for 0 to 5 percent of the total resonant absorption and that its parameters are only poorly determined. In addition, even small deviations in the line shape of doublet A from Lorentzian shape will markedly affect the numerical values obtained for the parameters of the overlapped doublet B. Only little significance should, therefore, be attached to these values.

The line widths for doublet A are generally in the range 0.29 to 0.35 mm sec^{-1}, i.e. rather close to the line width of a Fe absorber (0.28 mm sec^{-1}) in the experimental setup used. The intensities for the two peaks of A are identical within the limits of error, indicating that the effect of preferred orientation within the powder sample is negligible. On the other hand, the half-widths of the B doublet are anomalous and the intensities are unequal, probably due to the large inherent errors mentioned above.

By comparison with the crystal structure determination (Stephenson and Moore 1968), the A doublet is assigned to Fe^{2+} in fivefold coordination, where it occurs mixed with Mg. The B doublet is supposedly due to ferric iron as concluded from the low isomer shift. Ferric iron is reported, though in small amounts, in all chemical analyses of grandidierite where separate determinations of ferrous and ferric species have been made. At the moment it cannot, however, be decided whether the small amount of ferric iron enters the five-coordinated R^{3+} position [Al(3)], the five-coordinated R^{2+} site (Mg), the octahedral positions Al(1) and Al(2) or even a tetrahedral position. The errors involved also prohibit a determination of ferrous/ferric ratios in grandidierite from the Mössbauer spectra.

In the four samples studied, a marked near-linear decrease of the quadrupole splitting with increasing $Fe^{2+}/(Fe^{2+}+Mg)$ ratio of the sample has been ob-

served (Fig. 2). A similar trend has been described for the high-iron site in cummingtonite (*M*4), orthopyroxene (*M*2, *cf.* Hafner and Ghose 1971) and for olivine (Bancroft *et al.,* 1967). This behaviour can be interpreted as increasing distortion of the site with increasing molecular fraction of iron in the sample. In this context it is important to note that in grandidierite the substitution of Fe^{2+} for Mg leads to an anisotropic inflation of the unit cell: whereas *c* and *a* remain essentially constant, *b* increases systematically with increasing iron component (Olesch and Seifert 1976). On the other hand, the quadrupole splittings of individual Fe^{2+} sites might also change as a function of nearby Fe concentration. This would imply that any "doublet" is actually a set of closely spaced doublets whose intensities change consistent with the numbers of types of local neighborhoods. The relatively narrow linewidths would, in terms of this model, indicate very similar quadrupole splittings. This would, however, be expected, since the fivefold (Fe^{2+},Mg) sites do not share polyhedral elements. This model could also account for the general broad-

ening of linewidths in the 77 K spectra relative to the 298 K spectra.

The effect of temperature on the hyperfine parameters of grandidierite has been studied in detail for sample 4 and is summarized in Figure 3. The quadrupole splitting (Fig. 3a) shows a marked nonlinear temperature dependence with a large change from liquid-nitrogen temperature to room temperature and a much slower decrease at higher temperatures. However, these effects cannot be evaluated at present, because they depend on the lattice contribution and the valence contribution to the quadrupole splitting, both of which are unknown. In the case of the highly distorted polyhedron around Fe^{2+} in grandidierite, the lattice contribution certainly cannot be neglected (*cf.* Huggins 1975). An additional complication results from the low symmetry of the site.

The temperature dependence of the isomer shift (Fig. 3b) was found to be practically linear at temperatures above 150°C, decreasing at a rate of 0.00071 mm sec^{-1} deg^{-1}. At lower temperatures the effect is smaller. Neglecting the intrinsic temperature depen-

Table 2. Hyperfine parameters of grandidierites

No.		1		2		3		4	
Source		Vohiboly		Sakatelo		Nampoana		Rhodesia	
Temperature, °K		77	298	77	298	77	298	77	298
χ^2 (512 channels)		523	452	554	699	728	638	652	534
Background x10⁻⁶		0.717	0.392	0.596	1.062	0.631	1.438	0.711	0.233
A_H**	I***	0497	0.491	0.484	0.477	0.475	0.475	0.476	0.479
	Γ†	0.323	0.298	0.314	0.296	0.301	0.289	0.334	0.320
A_L	I	0.503	0.509	0.470	0.468	0.458	0.477	0.475	0.472
	Γ	0.372	0.348	0.307	0.290	0.313	0.296	0.350	0.319
B_H	I	–	–	0.015	0.022	0.034	0.024	0.025	0.015
	Γ	–	–	0.196	0.323	0.181	0.197	0.276	0.197
B_L	I	–	–	0.031	0.034	0.034	0.024	0.025	0.034
	Γ	–	–	0.423	0.361	0.181	0.197	0.276	0.450
Δ (A)††		1.947	1.746	1.906	1.724	1.882	1.712	1.856	1.681
δ (A)†††		1.231	1.101	1.231	1.106	1.222	1.101	1.230	1.099
Δ (B)††		–	–	1.229	1.201	1.172	1.133	1.328	1.252
δ (B)†††		–	–	0.417	0.333	0.439	0.334	0.424	0.365
$I_A/(I_A+I_B)$		–	–	0.954	0.944	0.932	0.951	0.951	0.951
$I_{AH}/(I_{AH}+I_{AL})$		0.497	0.491	0.508	0.505	0.509	0.499	0.500	0.504
mg Fe/cm²		1.13	1.13	1.56	1.56	1.21	1.21	2.68	3.83

* Sample numbers correspond to Table 1.

** The indices H and L refer to the high- and low velocity peak, respectively.

*** Intensities normalized to total intensity = 1.000.

† Full width at half height, in mm sec^{-1}.

†† Quadrupole split in mm sec^{-1}, e.s.d. 0.005.

††† Isomer shift relative to metallic iron.

In the two spectra of sample 3 and the 77 °K spectrum of sample 4 the intensities and half widths of doublet B have been constrained to be equal.
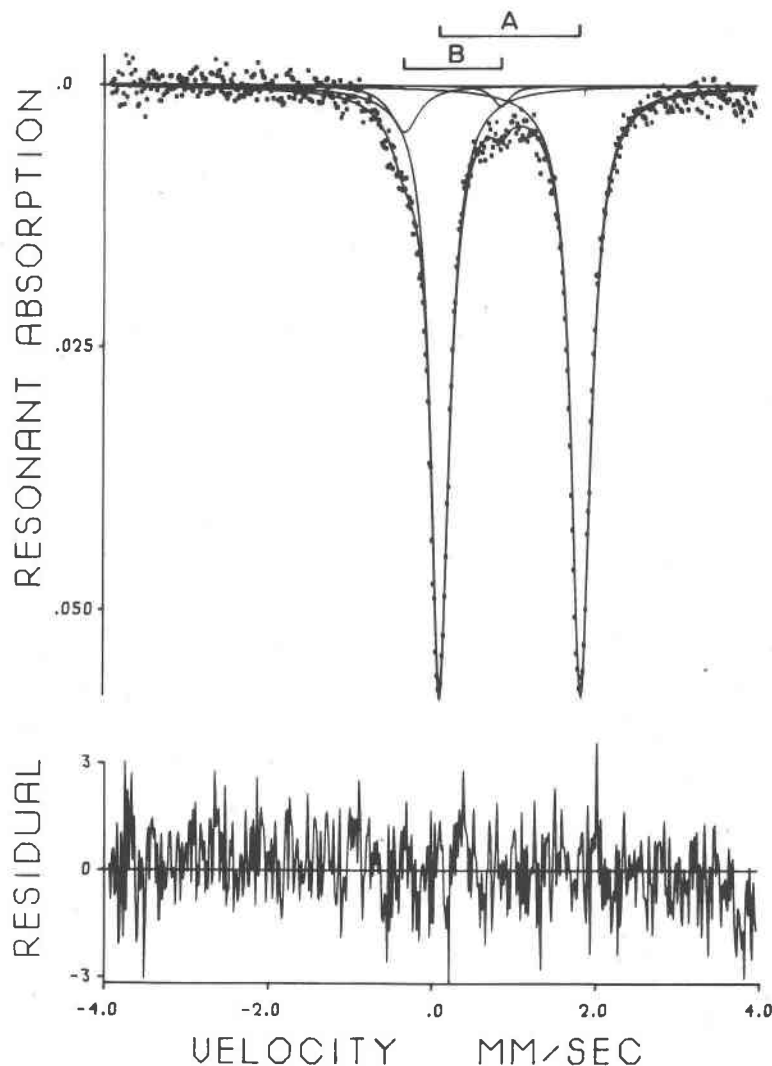
Fig. 1. Mössbauer spectrum of grandidierite (sample 2, Table 1) taken at 298 K. The solid line is a least-squares fit assuming four Lorentzians (twelve line variables, one background variable). The deviations of the solid line from the data (divided by the square root of the background) are plotted below the spectrum. The doublet designated A corresponds to Fe^{2+} in fivefold coordination and that designated B to Fe^{3+}.

dence of the isomer shift of Fe^{2+} that is only in the order of 10^{-6} to 10^{-5} mm sec^{-1} deg^{-1} (Hazony 1973), the data can be interpreted by the second-order Doppler shift. Using the formalism put forward by Clark et al. (1967, equ. 23b) but modified for the isotropic case, we obtained an optimum fit between observed and calculated isomer shifts with $\delta = 1.339$ mm sec^{-1} and a Debye temperature of 300 ± 50 K. The use of an isotropic model is justified by the observation of Stephenson and Moore (1968) that the root-mean-square displacements calculated from the X-ray data are spherical within the limits of error.

Discussion: Hyperfine parameters of Fe^{2+} in fivefold coordination

The following silicates are known to contain part or the entire divalent iron in a fivefold coordination: grandidierite, vesuvianite, rhodonite, pyroxmangite, and pyroxferroite. No Mössbauer data exist for pyroxmangite, and the assignment of peaks to the (5+1) coordinated position cannot be made unambiguously in pyroxferroite because of considerable overlap of several peaks (Dowty and Lindsley 1974). Divalent iron in a fivefold coordination has also been claimed

by Duncan and Johnston (1974) to occur in cordierite. An alternative explanation (electron hopping mechanism involving octahedral and tetrahedral Fe only) of the Mössbauer spectrum of cordierite has been put forward by Pollak (1976), and is preferred here because of its consistency with optical absorption spectra.

Table 3, therefore, gives hyperfine parameters of vesuvianite, rhodonite, and grandidierite only, in addition to parameters obtained for a square planar and two different octahedral environments for comparison. Qualitatively, the sequence from left to right in Table 3 can be interpreted as increasing distortion from an octahedral coordination. In accordance with the well-known empirical relationship between coordination or geometry of a site and the quadrupole splitting, it is seen that this parameter decreases systematically from a slightly distorted octahedron to a square planar coordination. The temperature dependence of the quadrupole splitting, on the other
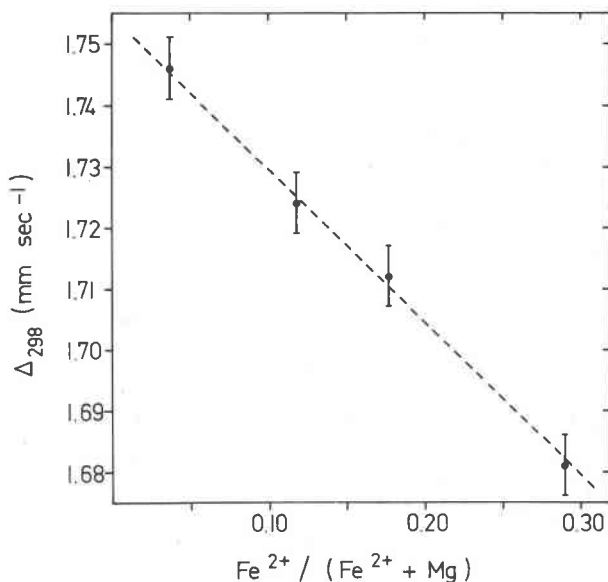

Fig. 2. Dependence of the quadrupole splitting (doublet A, at 298 K) on the $Fe^{2+}/(Fe^{2+}+Mg)$ molecular ratio of grandidierite. For discussion see text.
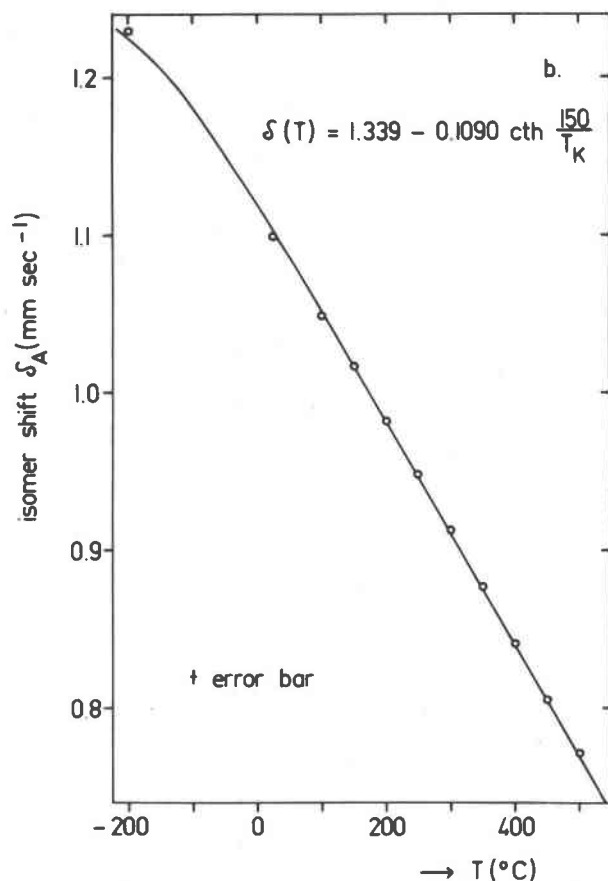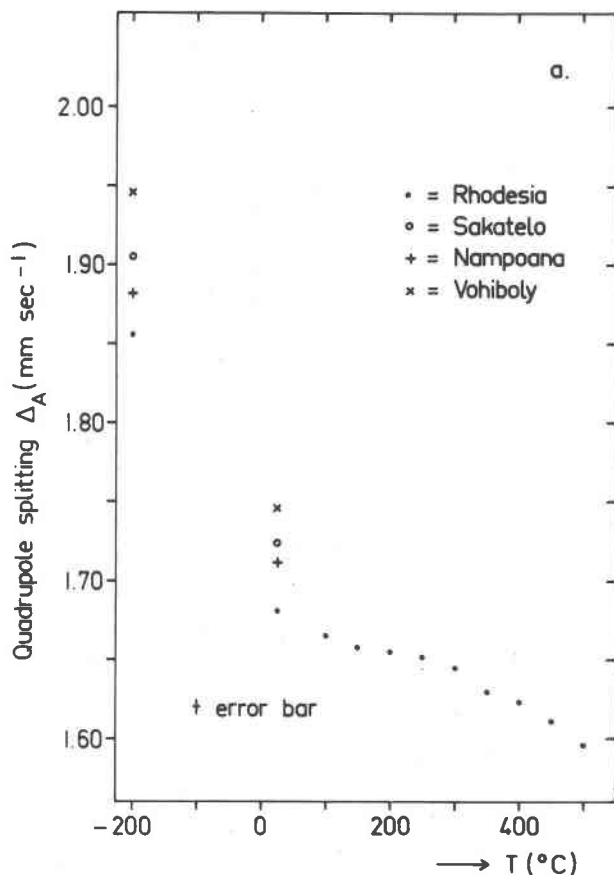

Fig. 3a,b. The temperature dependence of hyperfine parameters of grandidierite. 3a: Temperature dependence of the quadrupole splitting for all grandidierite samples studied. 3b: Temperature dependence of the isomer shift in sample 4, Table 1. The solid line represents a fit with $\delta = 1.339$ mm sec^{-1} and $\theta = 300$ K. For discussion see text.

Table 3. Hyperfine parameters of $^{57}Fe^{2+}$ in various coordination polyhedra, and their temperature dependence

Mineral	Orthopyroxene		Grandidierite	Rhodonite	Vesuvianite	Gillespite
Coordination of Fe^{2+} by oxygen	slightly distorted	strongly octahedron	trigonal bipyramid	tetragonal pyramid	tetragonal pyramid	square planar
Source	Burnham et al., 1971 M1	M2	this study, sample 2	Dickson 1975 sample A	Manning et al. 1975, Leurel	Clark et al., 1967
Δ^{**}	2.48	1.96	1.72	1.27	0.37	0.51
$\dfrac{(\Delta_{298} - \Delta_{77})^{\dagger}}{221}$	-2.89	-0.37	-0.93	-2.20	n.d.	-0.22
$\delta^{**,\dagger\dagger}$	1.17	1.13	1.11	1.08	0.84	0.75
$\dfrac{(\delta_{298} - \delta_{77})^{\dagger}}{221}$	-0.55	-0.60	-0.57	-0.52	n.d.	-0.41

*   The columns are arranged in the order of increasing distortion from octahedral symmetry.
**   At room temperature, in mm sec^{-1}.
†   In mm sec^{-1}deg^{-1} x 10^3.
††   Relative to metallic iron.
n.d. = not determined.

hand, does not follow such a simple trend, probably because it is the net result of two opposing effects, the lattice contribution and the valence contribution to the electric field gradient. Similar to the quadrupole splitting, the isomer shift decreases from left to right in Table 3 and, although less clearly, so does its temperature dependence. In terms of the Debye model this indicates looser bonding (lower isotropic Debye temperatures) in the less distorted sites (*cf.* Hafner and Ghose 1971).

Acknowledgments

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