

Local states of Fe²⁺ and Mg²⁺ in magnesium-rich olivines

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Abstract

⁵⁷Fe Mössbauer spectra of a synthetic forsterite and of one natural olivine were studied at temperatures between 4.2 and 1223 K. Spectra were also taken at pressures between 1 and 30 kbar at 568 K and in external magnetic fields between 4 and 7 T at 295 K and 4.2 K. The signs of the electric field gradient at M1 and M2 are positive. The average value of the two asymmetry parameters η is 0.20 ± 0.05 . The force constants of Fe²⁺ at M1 and M2 are 4.7 ± 0.1 eV/Å² and 4.2 ± 0.1 eV/Å², respectively. The axial splitting δ is 1120 ± 50 cm⁻¹ for both sites. The comparison of the ⁵⁷Fe data with the previous ²⁵Mg data allows a more detailed analysis of total, lattice, and Fe²⁺ valence field gradients at the M1 and M2 sites. The observed apparent lack of site preference for Fe²⁺ can be interpreted in terms of the local electronic properties.

Introduction

Many physical properties of olivines (Fe,Mg)₂SiO₄ are determined by the local states of bonding at the atomic positions and their dependences on temperature and pressure. The crystal structures of olivines are orthorhombic with space group *Pnma*. In this paper we are particularly concerned with the local properties of the positions of the bivalent cations, Fe²⁺ and Mg²⁺, which are octahedrally coordinated. There are two distinct positions, M1 and M2, with point symmetries $\bar{1}$ and *m*, respectively. The distribution of the Fe²⁺ and Mg²⁺ ions is generally disordered over M1 and M2, although possible preferences of Fe²⁺ for M1 or M2 under certain conditions have been debated in the past. Many questions, particularly the cationic exchange between M1 and M2 at elevated temperatures and its kinetics are still open. However, for the interpretation of such processes, detailed studies of the local site properties are desirable.

In the past, Mössbauer spectroscopy of ⁵⁷Fe has been mainly used for studying iron rich olivines (Eibschütz and Ganiel, 1967; Kündig et al., 1967; Bush et al., 1970). In the present work we describe Mössbauer studies of synthetic and natural olivines with low concentrations of iron (0.0025 and 0.1 mol. fraction). The experiments were carried out in a wide range of temperatures (4.2–1223 K), at high external fields (4–7 T), and at high pressure (30 kbar) and elevated temperature (568 K).

In this paper, the measured magnitudes, signs, and asymmetries of the electric field gradient (EFG) tensors of ⁵⁷Fe in forsterite are compared with the ²⁵Mg nuclear

magnetic resonance data previously obtained for the same mineral (Derighetti et al., 1978) and with theoretical EFG calculations. Such comparison is interesting in view of the relationship between lattice and valence contributions to the total EFG. This may be a step towards a more general consideration of local structure and chemical bonding. In particular, the estimated axial field splittings of the iron 3*d* orbitals can tentatively explain the weak, if any, preferential site occupancy by Fe²⁺ ions, which appears to be independent of the external state during the crystallization of olivine.

The Mössbauer spectra, if measured over a wide temperature range, also supply information about the dynamics of Fe²⁺ ions. For this, the estimated Debye temperatures and force constants for both sites may be compared with X-ray diffraction studies at high temperatures and high pressures provided that sufficiently refined data are available.

Samples

Two magnesium-rich olivines with the following compositions were studied. Sample (1): (Fe_{0.0025}Mg_{0.9975})₂SiO₄. This forsterite sample was obtained by powdering a single crystal specimen of high perfection grown using the Czochralski method. High enrichment of ⁵⁷Fe (90.4%) permitted the recording of Mössbauer spectra with a high total resonant absorption effect of 18% despite the low concentration of iron. Sample (2): (Fe_{0.01}Mg_{0.99})₂SiO₄. This sample was kindly provided by T. Malysheva. It was a high temperature olivine separated from a natural garnet peridotite.

The absorbers for the measurements at 295, 78 and 4.2 K were made by mixing powdered samples with lucite powder. Pellets with a diameter of 12 mm were prepared by heating at 420 K and pressing at 2 kbar for 30 minutes. For high temperature measurements the samples were mixed with boron nitride and distributed homogeneously on an iron-free beryllium plate, also 12 mm in diameter. The absorber thickness was about 0.1 mg

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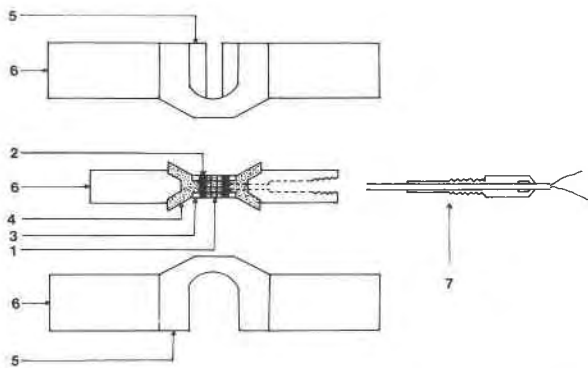


Fig. 1. Design of the high pressure, high temperature cell. (1) sample, (2) graphite heater, (3) copper connection, (4) pyrophyllite filler, (5) B_4C anvils, (6) stainless steel rings, (7) thermocouple in Al_2O_3 tube fixed in a steel screw.

$^{57}\text{Fe}/\text{cm}^2$ for sample (1) and about $4 \text{ mg Fe}/\text{cm}^2$ for sample (2) so that the samples could be approximately treated as "thin" absorbers.

Measurements

The Mössbauer spectra in the temperature range between 295 and 1223 K were recorded using a vertically operating, water cooled furnace with a tungsten filament. The vacuum during the measurements varied from 5×10^{-5} to 10^{-3} Torr, depending on the temperature which was stabilized within 2 K.

Measurements in high, external magnetic fields were carried out using a superconducting solenoid which allowed the taking of spectra at liquid helium, liquid nitrogen, and room temperatures. The direction of the gamma rays was parallel to the magnetic field. The source was kept at a "zero field" position 4 cm from the absorber. This fortunate source-to-absorber geometry was possible due to a field compensation coil in the solenoid at the side of the source. However, the experimental line width in the absorber was generally broadened to widths of about 0.28 mm/s probably due to the fact that the magnetic field at the source was not exactly zero.

The apparatus used for the measurements of Mössbauer spectra at high pressures was the equipment described by Amthauer et al. (1979) modified for high temperature work up to 600 K. This temperature is needed for obtaining the resolution of the distinct quadrupole splittings of ^{57}Fe at M1 and M2. The investigated sample was mixed with BN powder, inserted into a graphite ring (4 mm in diameter), and pressed between two B_4C anvils. The current through the graphite ring, being the main heating element, was 40 A at 500 K. The temperature of the sample was measured by a Pt-Pt (10% Rh) thermocouple, which was used also for temperature regulation (± 2 K). The correction for the pressure-induced change of the thermoelectrical voltage given by the thermocouple was considered (Bundy and Strong, 1962). The pressure vs. applied force calibration was carried out at room temperature using the known resistivity jumps of bismuth at 25.4 and 27 kbar (Bundy and Strong, 1962) and of ytterbium at 40 kbar (Drickamer, 1965). The constant force during experiments was supplied by an automatically regulated hydrostatic press. Thus, there was no change in pressure during heating from 300 to 500 K.

The design of the high pressure, high temperature cell which has not been published before is shown in Figure 1. High pressure,

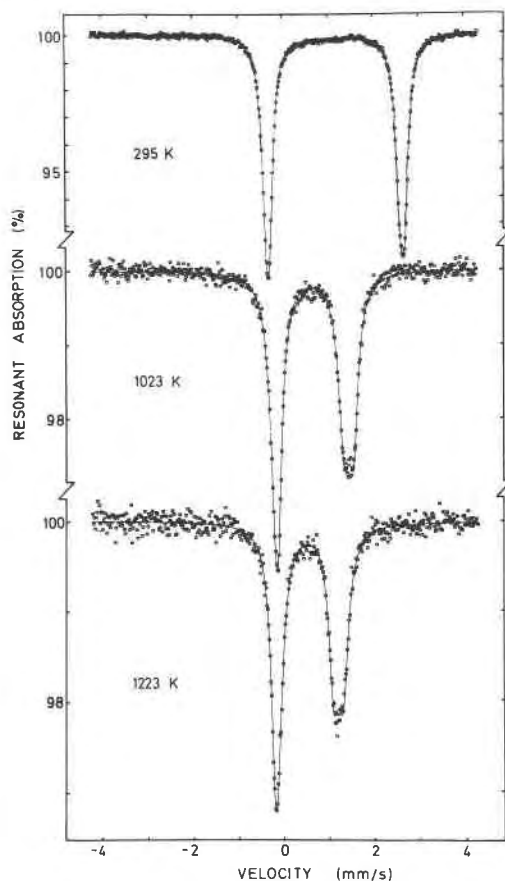


Fig. 2. Mössbauer spectra of ^{57}Fe in polycrystalline forsterite at temperatures as marked. The solid lines are Lorentzian line fits with widths and intensities constrained to be equal for the low and high velocity peaks of each doublet.

high temperature Mössbauer spectroscopy measurements have been attempted using a diamond cell heated with a laser beam (Ming and Bassett, 1974). The advantage of our design is that it yields undistorted spectra based on thin absorbers with reasonably large areas. However, the range of temperatures at present is limited to about 700 K due to the thermal properties of stainless steel (Thyrodur 2709) gasket.

All experiments were performed using a single-line source of ^{57}Co in metallic Pd or Rh matrices. The activity of the source varied from 20 to 40 mCi in the different experiments. The instrumental line width was smaller than 0.25 mm/s. The velocity scale in the Mössbauer spectra was calibrated by use of a metallic iron absorber.

Experimental results

Measurements at high temperatures

The temperature dependence of the Mössbauer spectra in forsterite doped with ^{57}Fe (sample 1) was investigated between 295 K and 1223 K. Spectra taken at 295, 1023 and 1223 K are shown in Figure 2. High temperature measurements were also carried out for the natural olivine ($\text{Fe}_{0.1}\text{Mg}_{0.9}\text{SiO}_4$ (sample 2).

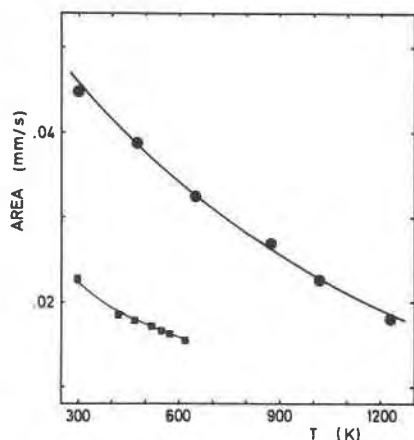


Fig. 3. Temperature dependence of the total area under the ^{57}Fe spectra of synthetic forsterite (sample 1; \bullet) and natural olivine ($Fe_{0.1}Mg_{0.9}$) $_2SiO_4$, (sample 2; \blacksquare). $\theta_D = 374 \pm 5$ K for forsterite and $\theta_D = 375 \pm 5$ K for natural olivine.

Since the two quadrupole-split Fe^{2+} doublets at the M1 and M2 positions of olivine strongly overlap, the fitting procedure is generally difficult. In our case, however, because of high crystal perfection and absence of any textural effects physically reasonable constraints can be assumed for the fit. Consequently, the spectra were fitted in three different ways with the constraints

$$W_L^1 = W_H^1, W_L^2 = W_H^2, I_L^1 = I_H^1, I_L^2 = I_H^2; \quad (a)$$

$$W_L^1 = W_H^1 = W_L^2 = W_H^2, I_L^1 = I_H^1, I_L^2 = I_H^2; \quad (b)$$

$$W_L^1 = W_H^1 = W_L^2 = W_H^2, I_L^1 = I_H^1 = I_L^2 = I_H^2. \quad (c)$$

Here W and I are the line widths and intensities, the superscripts 1 and 2 refer to the M1 and M2 sites, and L and H are the low and high energy lines, respectively, of the doublets. The final values for the quadrupole splitting QS , isomer shift IS and area A are the averaged results obtained from these fits. The errors given include the differences between the different schemes of fitting. The data on the temperature dependencies of the total areas

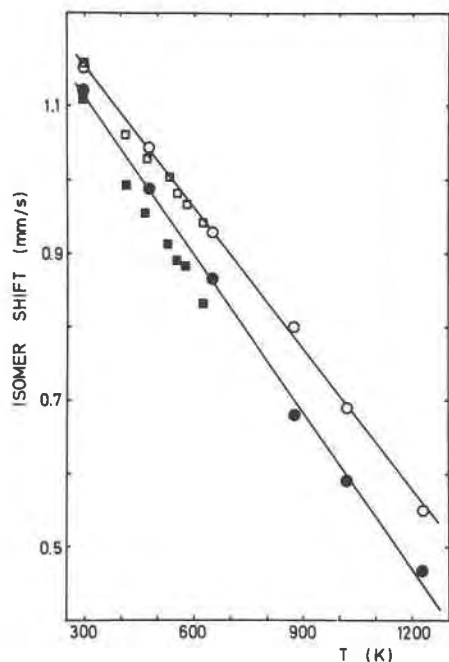


Fig. 4. Temperature dependence of the ^{57}Fe thermal shifts in synthetic forsterite (sample 1). The solid lines represent least squares fits based on equation (2), yielding force constants $K1 = 4.7$ eV/ \AA^2 (M1, solid points), $K2 = 4.2$ eV/ \AA^2 (M2, open points). The solid and open squares show the temperature dependence of the thermal shifts for ($Fe_{0.1}Mg_{0.9}$) $_2SiO_4$ (sample 2) (they were not included in the fit).

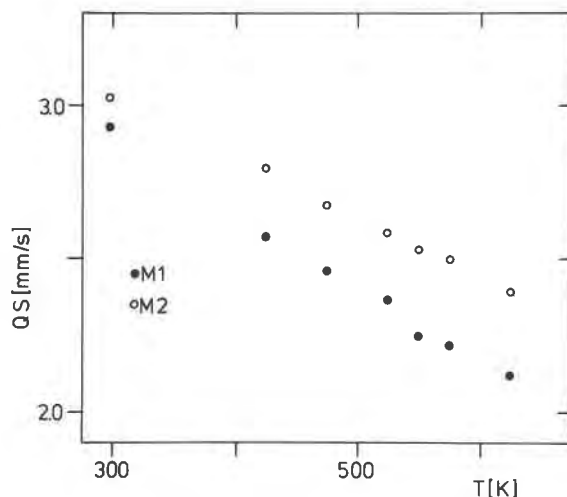


Fig. 5. Temperature dependence of the QS of ^{57}Fe at M1 (solid points) and M2 (open points) in natural olivine ($Fe_{0.1}Mg_{0.9}$) $_2SiO_4$ (sample 2).

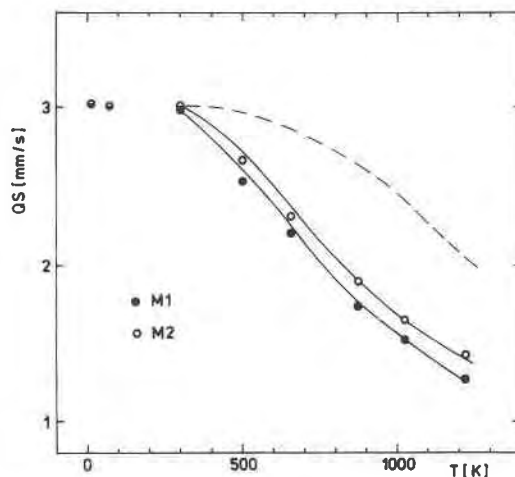


Fig. 6. Temperature dependence of the QS of ^{57}Fe at M1 (solid points) and at M2 (open points) in synthetic forsterite (sample 1). The solid lines are the least squares fits based on equation (3) and equation (7) yielding $\delta = 1120 \pm 50$ cm^{-1} for both positions. The dashed line is the calculated temperature dependence of QS for $\delta = 1860$ cm^{-1} reported by Burns, 1970. The QS values at 4.2 K and at 78 K were not included into the fit.

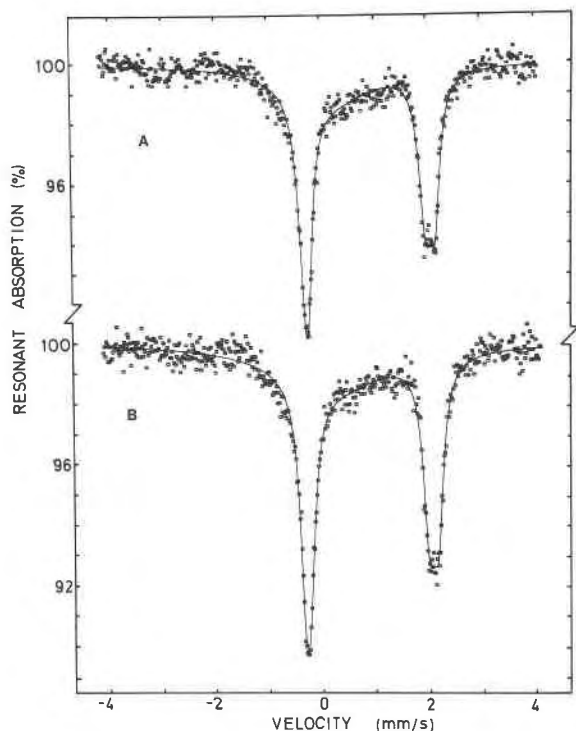


Fig. 7. Mössbauer spectra of forsterite at 1 bar (A) and 30 kbar (B) at 568 K. The spectra were not corrected for the background count rate produced by the iron impurities in the B₄C anvils.

under the spectra are shown in Figure 3, the thermal shifts are presented in Figure 4, and the temperature dependencies of the quadrupole splittings QS are plotted in Figures 5 and 6.

The spectra of synthetic forsterite (sample 1) taken at two different pressures at 568 K are shown in Figure 7. An increase of 10% of the total area of absorption lines was observed, but the spectra did not show any measurable change in QS.

While the overlap of the M1 and M2 paramagnetic doublets in olivines is nearly complete between 4 and 295 K, a distinct separation of the doublets occurs at temperatures higher than 500 K. QS plots from a larger number of spectra at temperatures between 295 and 623 K (Fig. 5) reveal that the temperature dependencies of the QS are almost linear over that range. There is no discontinuity at any temperature. First, the areas of the doublets will be analyzed in more detail. In the higher temperature limit, i.e., for $T \geq 0.5\theta_D$ where θ_D is the Debye temperature, the decrease of the total area A under the absorption spectrum of a thin absorber depending on temperature can be expressed as

$$A = C \cdot f_a = C \times \exp\left(-\frac{6E_R T}{K_B \theta_D^2}\right) \quad (1)$$

where E_R is the recoil energy of the nucleus (1.95×10^{-3} eV for ⁵⁷Fe), f_a is the recoil free fraction of the absorber, and C is a constant.

The least squares fit of equation (1) to our data is shown in Figure 3. The fit yielded $\theta_D = 374 \pm 5$ K for synthetic forsterite (sample 1) as well as for natural olivine (sample 2). In our case, the ratio of A at M1 and M2 turned out to be independent of T within a fitting error of 2% so that θ_D may be assumed to be the same for iron at both sites. This assumption is in agreement with earlier results (Bush et al., 1970) obtained for fayalite, an iron-rich olivine, and a magnesium-rich olivine. In that work it was also concluded that the recoil free fraction of iron at the M1 and M2 positions was the same within 2%.

The high temperature Mössbauer spectra also supplied values for the force constants of the Fe²⁺ ions at the M1 and M2 positions. In the higher temperature limit the thermal shift, i.e., the temperature dependence of the shift of the Mössbauer spectrum may be approximated (Gupta and Lal, 1972) by

$$\frac{\partial IS}{\partial T} = -\frac{3\hbar^2}{2ME_\gamma^2} K \frac{\partial \ln f_a}{\partial T} \quad (2)$$

Here, E_γ is the energy of the gamma transition (14.4 keV), M is the mass of ⁵⁷Fe, $M = 9.465 \times 10^{-26}$ kg, and K is the force constant. Substituting f_a obtained from the temperature dependence of the resonant area and fitting the experimental IS for each doublet, $K(M1) = 4.7 \pm 0.1$ eV/Å² (7.45×10^4 dyn/cm²) and $K(M2) = 4.2 \pm 0.1$ eV/Å² (6.66×10^4 dyn/cm²) are obtained. The fits together with the experimental IS values are shown in Figure 4.

Measurements of forsterite in high, external magnetic fields

The main purpose of measuring Mössbauer spectra in high, external magnetic fields H was the determination of the sign of the principal component V_{ZZ} of the EFG tensor³ at the M1 and M2 positions. Such spectra also allow us to estimate the asymmetry parameter η ; $\eta = (V_{XX} - V_{YY})/V_{ZZ}$, where V_{XX} , V_{YY} and V_{ZZ} are the values of the second derivative of the electrostatic potential V at the crystallographic positions of ⁵⁷Fe, and X, Y, Z refer to the diagonalized system.

The sign of V_{ZZ} and value of η were found by comparison of the experimental spectra with those computed by means of the "Gabriel-Ruby" program for calculating combined quadrupole and magnetic hyperfine interactions in polycrystalline samples (Gabriel, 1965; Collins and Travis, 1967). The magnitudes of the quadrupole splittings observed in zero-field spectra and experimental line widths of 0.28 mm/s were introduced as fixed parameters. Since the spectrum consists of two overlapping doublets due to

³ Cf. Discussion.

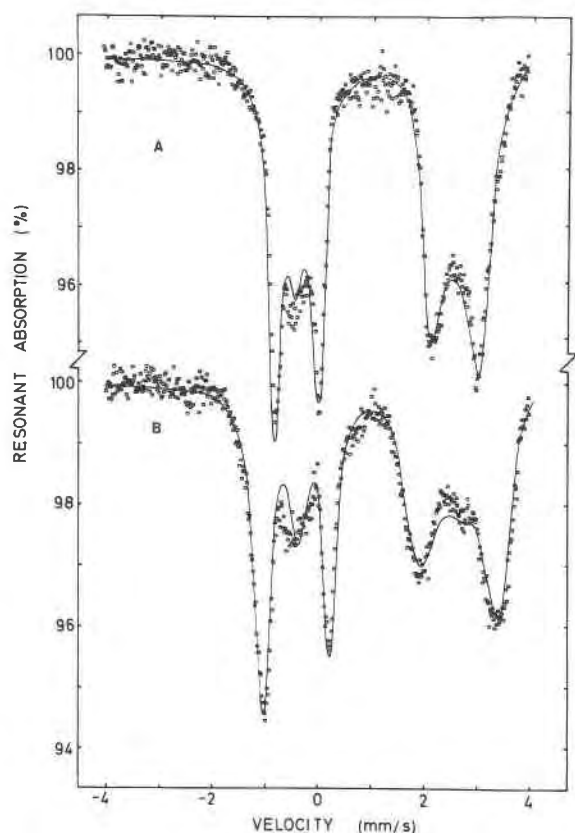


Fig. 8. Computed (solid line) and experimental (dots) ⁵⁷Fe spectra in polycrystalline forsterite in external magnetic fields of 4.0 T (A), and 6.0 T (B) at 295 K. The field was parallel to the gamma rays. For the computed spectra, $\eta = 0.2$ and a positive sign of V_{zz} were assumed.

Fe²⁺ at the M1 and M2 sites various simulations of spectra had to be computed using positive and negative signs of V_{zz} as well as different η values for both sites and different external magnetic fields. η was varied between 0 and 1 in steps of 0.05. The simulations showed that the spectrum depends on η and the sign of V_{zz} most critically at fields between 4 and 7 T. The best agreement between experimental and computed spectra was obtained for a positive sign of V_{zz} at the M1 as well as the M2 sites, and an average $\eta = 0.20 \pm 0.05$. Two experimental and computed spectra for fields $H = 4.0$ T and 6.0 T are shown in Figure 8.

The application of the Gabriel-Collins procedure used for the evaluation of Mössbauer spectra needs further comment. It is only correct for diamagnetic ions, or for paramagnetic ions which have isotropic properties as, for example Fe³⁺. Fe²⁺ in forsterite is, however, anisotropic, i.e., the effective magnetic field at ⁵⁷Fe, H_{eff} , is not parallel to the external field H . Its magnitude depends on the orientation of the crystal with respect to the external field. In this case a phenomenological model which describes the Mössbauer spectrum of paramagnetic powders in high

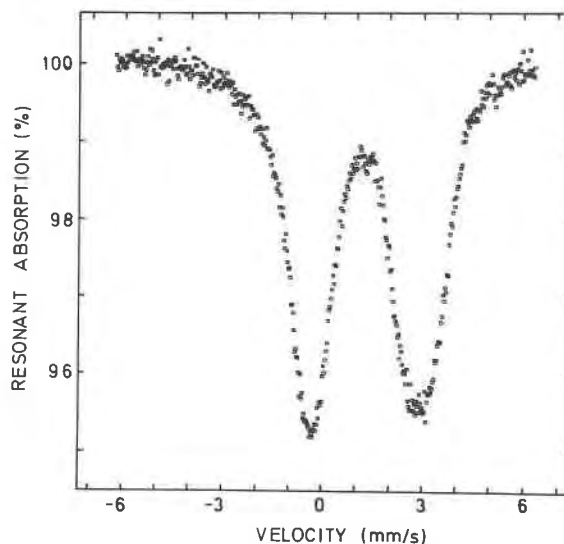


Fig. 9. ⁵⁷Fe spectrum in polycrystalline forsterite at 4.2 K in an external magnetic field of 7.15 T parallel to the transmitted gamma rays.

magnetic fields developed by Varret (1976) may be applied. It is based on the assumption that H_{eff} acting at the Fe²⁺ nucleus can be described as

$$H_{\text{eff}} = (1 + \tilde{B})H \quad (3)$$

where \tilde{B} is the "magnetization hyperfine tensor." Such magnetization effects become significant at low temperature and at the high field limit, when saturation of the magnetization in the easy direction appears. This can drastically change the line shape of the Mössbauer absorption. Such an approach has been successfully used for the description of ⁵⁷Fe spectra of Fe and Zn fluorosilicates studied in external fields (Varret, 1976).

For a verification of the data obtained, an additional experiment at $H = 7.15$ T and 4.2 K was made. The spectrum obtained, shown in Figure 9, consists of two broad lines and can not be reproduced by the simple method used in this paper due to enhanced magnetic anisotropy of Fe²⁺ at lower temperatures as discussed above. In consequence, this result supplied no independent estimate for the η value (the sign is obvious from room temperature spectra).

It is to be noted that the sign of the V_{zz} component of the EFG tensor as well as the asymmetry parameter for Fe²⁺ in forsterite are the same at both sites as in fayalite, Fe₂SiO₄. The components of EFG tensor in fayalite ($V_{zz} > 0$ and $\eta = 0.2$ at M1 and M2 sites) were estimated by Kündig et al. (1967) on the basis of the Mössbauer spectra of the magnetically ordered state at 4.2 K.

A drastic difference is observed, however, between the EFG measured at Fe²⁺ and at Mg²⁺ ions in forsterite. The components of EFG tensors at Mg²⁺ in forsterite have been precisely determined by Derighetti et al. (1978) by

means of magnetic resonance on dynamically polarized ²⁵Mg nuclei in a single crystal. The given values of the asymmetry parameters are larger: 0.4 at M2 and 0.96 at M1. The signs of the main EFG components were not determined experimentally but a calculation based on the point charge model including ionic, dipole and quadrupole contributions as well as overlap effects lead to positive signs (Rager and Schmidt, 1981). These results, together with our data are the basis of the discussion of the relationship between lattice and valence EFG, presented in the next section.

Discussion

Correlation between lattice and valence field gradient

A primary interest of this study was the relation between the EFG tensors of ⁵⁷Fe and ²⁵Mg (Derighetti et al., 1978) at the two nonequivalent M1 and M2 sites. The ⁵⁷Fe tensors are described in their principal axes system X,Y,Z and consist of two contributions: (1) the dominating valence contribution V_{ij}^v with the principal axes system X*,Y*,Z* and (2) the lattice contribution V_{ij}^l with the principal axes system x,y,z. According to the model of Ingalls (1964) it is usually assumed that the systems X,Y,Z, X*,Y*,Z* and x,y,z have identical orientation. For the ²⁵Mg tensor, of course, V_{ij}^v is assumed to be zero, i.e., V_{ij}^v = V_{ij}^l. A discussion of the signs of the various tensors and the different orientations of their principal axes appears worthwhile.

For comparing the lattice tensors acting on ⁵⁷Fe and ²⁵Mg with the total tensors, the data should be corrected for the different Fe²⁺ and Mg²⁺ Sternheimer antishielding factors γ_∞. Thus at ⁵⁷Fe the lattice tensor is

$$V_{ii}(\text{Fe}^{2+}) = \frac{[1 - \gamma_{\infty}(\text{Fe}^{2+})]}{[1 - \gamma_{\infty}(\text{Mg}^{2+})]} \times V_{ii}(\text{Mg}^{2+}) \quad (4)$$

where γ_∞(Mg²⁺) = -3.5 (Schmidt et al., 1979), γ_∞(Fe²⁺) = -10.972 (Sternheimer, 1972), and i = x,y,z. Assuming a positive sign of V_{zz}(Mg²⁺) (Rager and Schmidt, 1981) and substituting the experimental data for V_{ii}(Mg²⁺) (Derighetti et al., 1978), yields the values for the ⁵⁷Fe lattice tensor components at both positions⁴ expressed in the principal axes system, x,y,z.

The estimation of the errors in V_{ii}(Fe²⁺) is difficult. The experimental errors of V_{ii}(Mg²⁺) are about 10¹⁹ V/m². The errors of calculated γ_∞(Fe²⁺) and γ_∞(Mg²⁺) are not known; they can even reach 10%, but this causes only systematic shifts of V_{ii}(Fe²⁺). In particular the value of the asymmetry parameter η is not affected.

However, the question of how much the lattice EFG measured on Mg²⁺ ions can be identified with the lattice EFG acting on Fe²⁺ at the same crystallographic position

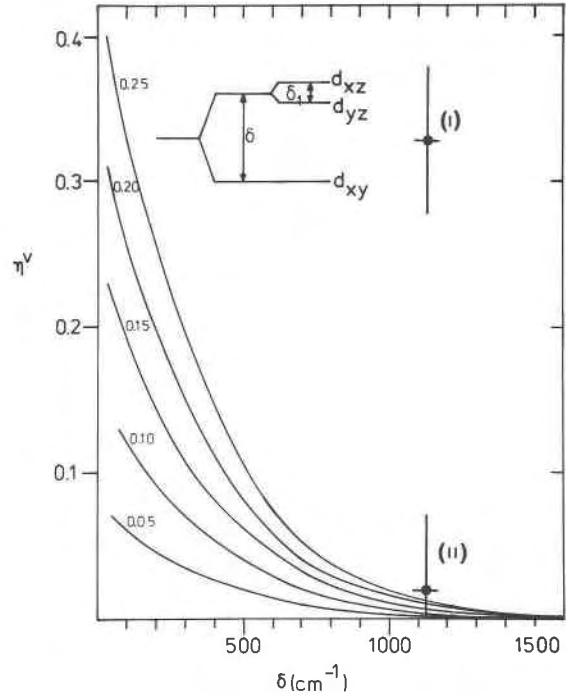


Fig. 10. The asymmetry parameter of a positive valence EFG calculated for 295 K in the function of the axial field splitting δ. The different lines refer to different δ_{xz}/δ_{yz} ratios, as marked. The experimental points (i) and (ii) result from two possible relative orientations of the valence and lattice EFG tensors.

is still open for discussion. The two gradients may differ because of the different overlap contribution, which at least in the Mg²⁺ case is meaningful (Rager and Schmidt, 1981).

For obtaining the valence EFG, V_{ij}^v, the lattice EFG tensor expressed in the x,y,z frame must be subtracted from the total EFG tensor. From a comparison of the data of Kündig et al. (1967) and Derighetti et al. (1978), it is found that at the M2 position V_{zz} is parallel to V_{yy}^l (the Z axis coincides with the y axis). For further discussion it is reasonable to assume that not only is Z parallel to y but also (1) z||Y and x||X, or, alternatively, (2) z||X, x||Y. Using the proper transformation matrix, describing the rotation by 90° around the x axis for case (1) and rotation by 90° around x and y axes for case (2) the V_{ij}^l tensor can be transformed to the X*,Y*,Z* axes system. By this procedure, V_{ii}^v = V_{ii} - V_{ii}^l (for i ≠ j, V_{ij}, V_{ji}, V_{ij}^v = 0).

The first transformation leads to a highly asymmetrical valence EFG tensor for Fe²⁺ with η^v = 0.33 and should be excluded from further discussion, according to the following considerations.

The asymmetry parameter of the valence tensor, η^v, of the Fe²⁺ ion in a distorted octahedrally coordinated site is caused by the unequal population of the 3d_{xz}, 3d_{yz} and 3d_{xy} levels. If the ground state of Fe²⁺ is 3d_{xy} the V_{zz} is positive. The η is determined by the temperature, by the

⁴ An energy shift of 1 mm/s for the 14.4 keV transition in the ⁵⁷Fe Mössbauer spectrum is equal to 11.625 MHz, or to 4.808 × 10⁻⁹ eV. An axial tensor of V_{zz} = 10²¹ V/m² produces a quadrupole splitting of ⁵⁷Fe of 0.208 mm/s (assuming Q = 0.20 × 10⁻²⁰ cm² for the quadrupole moment of 14.4 keV state of ⁵⁷Fe).

Table 1. The components of the lattice (1), total and valence (v) EFG tensors in M1 and M2 sites, expressed in the total EFG tensor principal axis system X,Y,Z in the units of 10²⁰ V/m²

| | V _{xx} ^l | V _{yy} ^l | V _{zz} ^l | V _{xx} ^v | V _{yy} ^v | V _{zz} ^v | V _{xx} ^v | V _{yy} ^v | V _{zz} ^v |
|----|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|
| M1 | +24 | -1 | -23 | -57 | -85 | +142 | -81 | -84 | +165 |
| M2 | +20 | -6 | -14 | -59 | -88 | +147 | -79 | -82 | +161 |

axial field splitting δ , and by the rhombic field splitting $\delta_1 = 12D$, where D is rhombic field parameter according to equation (5) (Ingalls, 1964)

$$\eta^v = \frac{3}{2} \frac{P|xz\rangle - P|yz\rangle}{1 - \frac{1}{2}(P|xz\rangle - P|yz\rangle)}$$

$$= \frac{3}{2} \frac{\exp\left[-\left(\delta - \frac{1}{2}\delta_1\right)/kT\right] - \exp\left[-\left(\delta + \frac{1}{2}\delta_1\right)/kT\right]}{1 - \frac{1}{2}\left\{\exp\left[-\left(\delta + \frac{1}{2}\delta_1\right)/kT\right] + \exp\left[-\left(\delta - \frac{1}{2}\delta_1\right)/kT\right]\right\}}$$
 (5)

where $P|yx\rangle$, $P|xz\rangle$, $P|xy\rangle$ are the populations of the $3d_{xy}$, $3d_{yz}$ and $3d_{xz}$ orbitals.

η^v was calculated as a function of δ for $T = 294$ K and for different δ_1/δ ratios. The result is shown in Figure 10. Assuming $\eta^v = 0.33$ (case (1)) leads to a δ of less than 300 cm⁻¹. Such small axial field splitting would lead to a very fast decrease of the quadrupole splitting with increasing temperature. This is inconsistent with our data (see the following section). In summary, we believe that case (2), i.e., $x\parallel Y$, $y\parallel Z$, $z\parallel X$, leading to a nearly axial valence tensor, must be chosen.

The discussion of the tensor at the M1 site is less straightforward. First, $\eta^l = 0.964$, i.e., $V_{zz}^l \cong -V_{yy}^l$, and the assignment of axes, as well as the discussion of the sign become irrelevant. Second, because of the crystallographic point symmetry $\bar{1}$ at M1, the systems X,Y,Z, and x,y,z do not coincide with any crystallographic axis. Moreover, the orientation of the total tensor obtained from Mössbauer measurements is subject to considerable error.

At any rate, according to Kündig et al. (1967) and Derighetti et al. (1978), the angle between Z and z or, alternatively, Z and y, is about 15°, i.e., the Z and z axes are nearly parallel. If the second orientation is arbitrarily chosen, i.e., Z parallel to y, V_{ij}^l at the M1 site may be treated as in the case of M2.

In Table 1 the components of the lattice (V_{ij}^l), valence (V_{ij}^v) and total (V_{ij}^t) tensors expressed in the X,Y,Z system are presented. The V_{ij}^t components are calculated from the data of Derighetti et al. (1978) using equation (4) and transformed to the X,Y,Z system. The V_{ij}^t values were obtained using the equation

$$QS = \frac{V_{zz}}{2} eQ \sqrt{1 + \frac{\eta^2}{3}} \quad (6)$$

where QS is the experimental quadrupole splitting, and $\eta = 0.2$ is the experimental value of the asymmetry parameter of the total tensor. Finally, $V_{ij}^t = V_{ij}^v - V_{ij}^l$.

Considering the data collected in Table 1, it can be concluded that in spite of the fact that the lattice tensor is highly asymmetric (especially at M1) the valence contribution to the total tensor is, at room temperature, fairly axial ($\eta^v = 0.018$, as estimated from Table 1) i.e., it is indicative of a big axial field splitting.

The experimental results on forsterite appear to weaken the prediction of Ingalls (1964) concerning the relation between the lattice and valence contributions to the total tensor (they should be of opposite signs and the x,y,z system should be identical with the X,Y,Z system).

Temperature dependence of the quadrupole splitting (QS) and the axial field splitting δ

The temperature dependence of the valence tensor of Fe²⁺ was described by Ingalls (1964). The ligand field parameters (cf. also Gibb, 1968) can be estimated from the decrease of the QS with the increasing temperature if the weakly temperature dependent lattice contribution is subtracted from the total tensor. In our present case, the lattice tensors in forsterite are, of course, known precisely at 4.2 K from the ²⁵Mg data of Derighetti et al. (1978). In olivines, two opposing contributions to the temperature dependence of the lattice tensor may be expected: (1) thermal expansion of the lattice may reduce the tensor with increasing temperature; (2) the increasing mean static distortion of the oxygen octahedra around M1 and M2 with increasing temperature (Smyth and Hazen, 1973; Smyth, 1975) may produce an increasing contribution to the tensor. This contribution may partly cancel or even outweigh (1).

For further discussion the high temperature (568 K) and high pressure (30 kbar) Mössbauer measurements should be included. It is known that the ratio of the coefficient of linear thermal expansion α , and the coefficient of linear compression β , are constant for a wide variety of minerals (Hazen, 1976, 1977). Thus the process of the thermal volume decrease is structurally similar to the decrease of volume during compression. For forsterite, a pressure difference of 30 kbar corresponds to a decrease of the average M-O bond of about 0.018 Å. The same decrease is achieved by a decrease in temperature of about 700 K (Hazen 1976). No pressure dependence of the QS was observed at 30 kbar (cf. Fig. 7). It can, therefore, be concluded that structural changes expected in our experimental temperature range (300–1220 K) have little influence on the lattice tensor, which can be assumed to be independent of temperature.

In the high temperature region, where the influence of spin orbital interaction on the tensor is negligible, the temperature dependence of an axially symmetric valence tensor V_{zz}^v , at an octahedrally coordinated site of Fe²⁺ (Ingalls, 1964) is

$$V_{zz}^v = -2V_{yy}^v = -2V_{xx}^v = C \times \frac{1 - \exp(-\delta/kT)}{1 + 2 \exp(-\delta/kT)} \quad (7)$$

Here $\delta = 3D_s$ is the T_{2g} orbital splitting, where D_s is the axial field parameter. The values of the total components V_{ii} can be calculated for any temperature as

$$V_{ii}(T) = V_{ii}^0(T) + V_{ii} \quad (8)$$

To obtain the explicit form of the temperature dependence of QS the $V_{ii}(T)$ components must be inserted into equation (6). The experimental values of QS are presented in Figure 6. The least squares fit of the function of equation (6) to the points of Figure 6 with the conditions described by equation (7) (solid lines in Fig. 6) leads to $\delta = 1120 \pm 50 \text{ cm}^{-1}$. This result is inconsistent with $\delta = 1860 \text{ cm}^{-1}$ (dashed line in Fig. 6) of Burns (1970). It should be noted, however, that the value of 1860 cm^{-1} results, at least for the M1 site, from a numerical error in subtracting the energy of 8060 cm^{-1} and 7200 cm^{-1} of the two absorption bands in the polarized absorption spectra of olivine (Burns, 1970). Our result can be related rather well to the absorption minimum of 1124 cm^{-1} in the infrared spectra of forsterite (Runciman et al., 1973).

Preferential site occupancy of bivalent iron in olivines

In view of the different point symmetries of the M1 and M2 positions and the somewhat different geometrical distortions of the M1 and M2 coordination octahedra a preference of Fe²⁺ is expected for one of the two positions, at least in general. The EFG tensors are distinct for the two positions, particularly at temperatures higher than 250°C. Moreover, the average M-O distance is somewhat shorter for M1 ($d = 2.095 \text{ \AA}$) than for M2 ($d = 2.131 \text{ \AA}$) (Wenk and Raymond, 1973), yielding a slightly smaller volume for the M1 octahedron.

The relative volumes of M1 and M2 octahedra are consistent with the result that the force constant $K(M1)$ is greater than $K(M2)$. This fact indicates that the Fe²⁺ ions at M1 are somewhat more tightly bonded to the oxygen ions than at M2. This result does not support the conclusion of Hazen (1976) that the compressibility of M1 octahedra is larger than that of M2. From our data for the force constants we find

$$\frac{\partial V(M2)}{\partial p} : \frac{\partial V(M1)}{\partial p} = \left(\frac{K(M1)}{K(M2)} \right)^3 \approx 1.4$$

In spite of the geometrical difference between the M1 and M2 octahedra the electronic levels of Fe²⁺ appear to be quite similar at both sites. This rather surprising result is confirmed by the spectra at high pressures. The hyperfine parameters are not influenced significantly by pressures up to about 30 kbar.

The ordering of cations may be discussed in terms of the crystal field stabilization energy CSFE. For octahedral coordination,

$$\text{CSFE} = \frac{2}{5}\Delta_0 + \frac{1}{3}\delta \quad (9)$$

where Δ_0 is the crystal field splitting and δ is the axial field splitting (Burns, 1970). In pyroxenes, it was concluded that the difference in δ at the M1 and M2 positions is

responsible for the preference of Fe²⁺ for the M2 position (Burns, 1970). The apparent lack of cation ordering in olivines appears to be related to the equal δ splittings of Fe²⁺ at both M positions as concluded from present data. Therefore, precise determination of Fe²⁺ ordering over M1 and M2 in the olivine solid solution by Mössbauer spectroscopy will require careful experimental study of the relative M1 and M2 resonant absorption areas over a large region of temperature.

The weak preferential site occupancy in olivines has also been explained by a dynamical Jahn-Teller effect (Welsch et al., 1974). However, in that work an incorrect order of t_{2g} level splitting was assumed, i.e., from the distortion of the M2 octahedron it was concluded that the ground state is a doubly degenerated ($3d_{xz}, 3d_{yz}$) level. The positive signs of V_{zz} show that the ground states must be $3d_{xy}$ singlets for both positions. Thus, the values of stabilization energy of Welsch et al. (1974) require reconsideration.

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