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A temperature-dependent single-crystal Raman spectroscopic study of fayalite: evidence for phonon-magnetic excitation coupling

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Abstract The polarized single-crystal Raman spectrum of synthetic fayalite, Fe_2SiO_4 , was recorded between 5 and 773 K in order to investigate its lattice dynamic behavior. A broad absorption envelope is observed at wavenumbers between 800 and 960 cm^{-1} and it contains two intense bands at 816 and 840 cm^{-1} at 293 K in the (*cc*) spectrum. The integral area of the envelope decreases upon cooling from 293 K and reaches a minimum around 55 K. It then increases again with a further decrease in temperature down to 5 K. It is proposed that the envelope in the (*cc*) spectra consists of seven different modes, some of which are symmetry-forbidden, that arise from combination scattering of nonsymmetric internal SiO_4 -stretching modes of B_{ig} symmetry ($i = 1, 2, 3$) and low-energy excitations. The individual modes can be observed under different polarizations and agree in number and wavenumber with those obtained by fitting the broad envelope with Lorentzians. An analysis of the Raman spectrum as a function of temperature, using the known magnetic properties of fayalite, allows the assignment of the low-energy excitations to short-range magnetic interactions. Modulation of the $\text{Fe}^{2+}(1)\text{--Fe}^{2+}(2)$ exchange energy leads to phonon-magnetic excitation coupling and the main role in the $\text{Fe}^{2+}(1)\text{--Fe}^{2+}(2)$ magnetic interaction occurs via superexchange through the oxygens. The magnetic excitations are not magnons in the usual sense, that is as quasiparticles having a long wavelength in an ordered system. The degree of observed broadening of the SiO_4 -stretching modes is consonant with a $\text{Fe}^{2+}(1)\text{--Fe}^{2+}(2)$ exchange energy of 4.7 cm^{-1}

presented by Schmidt et al. (1992). At temperatures above 300 K the line width of the mode at 840 cm^{-1} decreases slightly, whereas those of low energy lattice modes increase. This suggests that a decrease in mode broadening due to weakened magnetic interactions compensates any thermally related broadening. Complete Fe^{2+} spin disorder may not be reached until at least 530 K. Results from this study show that estimates of third-law entropies for silicates using simple crystal-chemical considerations that do not account for magnetic properties cannot give accurate values for many transition-metal-containing phases.

Keywords Fayalite · Raman spectroscopy · Magnetic excitations · Lattice dynamics · Thermodynamic properties

Introduction

The Raman spectrum of fayalite, Fe_2SiO_4 , is different in appearance from the spectra of other isostructural olivines. This is notable in the high-wavenumber region, where a very broad envelope between 800 and 960 cm^{-1} consisting of internal SiO_4 -stretching vibrations occurs. For example, at ambient temperature the line width (i.e., FWHH) of the mode at 816 cm^{-1} is about 1.5 times and the mode at 840 cm^{-1} about 3.5 times larger than the equivalent modes in forsterite, Mg_2SiO_4 , or tephroite, Mn_2SiO_4 . This broadening, which has been observed before (Chopelas 1991), could therefore be related to Fe^{2+} and its magnetic properties in the olivine structure. However, there has been no experimental investigation of this spectral phenomenon which could be important for understanding the lattice dynamic and thermodynamic properties of fayalite and Fe–Mg olivine solid solutions. In general, one can state that little research has been done on rock-forming silicates with regard to magnetic properties and their effect on lattice dynamics. This is a poorly understood subject that has received little study in spite of the importance it has for all

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transition-metal-bearing silicates and their thermodynamic properties.

The static magnetic properties of fayalite have been investigated a number of times over the past 40 years. Santoro et al. (1966) determined, using powder magnetic susceptibility measurements, that a paramagnetic to antiferromagnetic phase transition occurs at 64.9 K (i.e., Néel temperature – T_N). Robie et al. (1982) observed in heat capacity measurements a sharp λ transition at 64.88 K corresponding to this inversion. Below T_N , the fayalite structure is magnetically ordered with the magnetic cell equal to the crystallographic cell in space group $Pnma$ (Ballet et al. 1989). The spins of Fe^{2+} at the M(2) site are parallel to the b axis, whereas Fe^{2+} at the M(1) site is antiferromagnetically coupled. Here, the spins are canted with respect to all three crystallographic axes at $T < T_N$ (Santoro et al. 1966; Fig. 1). The canting angle between the magnetic moment of Fe^{2+} on the M(1) site and the b axis increases from about 16° at 50 K to 40° at 10 K (Lottermoser et al. 1986; Fuess et al. 1988). Above T_N short-range magnetic order has been experimentally observed at least to 80 K (Krause et al. 1995) or 130 K (Robie et al. 1982). One can conclude, as a result of these different studies (see also Lottermoser et al. 1996; Ehrenberg and Fuess 1993), that the static magnetic properties of fayalite are well understood in terms of experiment and theory.

Fayalite's lattice dynamic behavior, on the other hand, is not so clear and uncertainties exist. In addition to Chopelas' Raman single-crystal study, Hofmeister (1987) made single-crystal IR measurements and model lattice-dynamic calculations on fayalite and concluded that complete Fe^{2+} spin disorder is not present below 680 K. She updated her room-temperature IR measurements in Hofmeister (1997). Price et al. (1991) measured the phonon density of states of fayalite at 17 and 300 K and observed spectral features around 160 cm^{-1} (20 meV) at low temperature that were thought to be related to magnetic excitations. Geick et al. (1991) undertook low temperature far-infrared measurements on fayalite and were able to measure six IR-active magnons occurring between 25 and 90 cm^{-1} under different magnetic field strengths. The results were

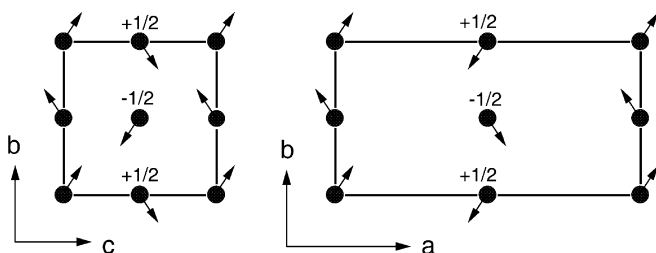


Fig. 1 Projection of the magnetic structure of Fe^{2+} on the M(1) site in fayalite, space group $Pnma$. The canting angle between the magnetic moment and the b axis is 16° at 50 K, for example, and it increases with decreasing temperature to 40° at 10 K. The spins of Fe^{2+} on M(2) are parallel to the b axis and are not shown. (Fuess et al. 1988)

treated in a spin-wave model. Schmidt et al. (1992) proposed that phonon–magnon coupling occurs based on their inelastic neutron scattering and far-infrared study that measured eight magnon dispersion curves having energies between 20 and 120 cm^{-1} (0.6 and 3.5 THz) at 11 K. They also presented magnetic-exchange constants for model spin-wave calculations that describe the interactions (see also Brotzeller et al. 1992).

The reason for the observed Raman-active SiO_4 -mode broadening needs to be investigated especially with respect to fayalite's magnetic properties. No measurements have been undertaken, however, at low temperatures. Therefore, we measured the polarized single-crystal Raman spectrum of fayalite in the temperature range from 5 to 293 K and also from 293 to 773 K to better understand its lattice dynamic and magnetic properties.

Methods

The synthetic fayalite crystal used for measurement is euhedral, doubly terminated and about 3 mm long and 2 mm across. It is brown in color. The crystal was grown in a FeCl_2 flux under an Ar atmosphere (F.Wallrafen, personal communication) and contains a very small amount of fine Fe particles.

Polarized Raman spectra were recorded with a Triplemate, SPEX spectrometer with a CCD detector, LN-1340PB, from Princeton Instruments. The 632.8-nm line of a He–Ne laser, having 50 mW output power, was used for spectral excitation. Spectra were obtained in 90° or 180° collection geometry. In the back-scattering geometry, the laser beam was focused to a diameter of $2\text{ }\mu\text{m}$ using a LD-EPIPLAN, 40/0.60 Pol., Zeiss objective. The spectral resolution at room temperature was 5 cm^{-1} , which is suitable to measure the broad modes observed in fayalite's spectrum. For the low-temperature measurements a resolution of 2 cm^{-1} was adopted. Low-temperature spectra were recorded by fixing the crystal on a cold finger of a helium cryostat from the company Air Products. The temperature of the cold finger in the cryostat was controlled with a precision of approximately $\pm 0.1\text{ K}$. However, the temperature accuracy directly on the sample could be not determined so well. Normally, the temperature on the crystal is higher than that recorded on the cold finger by up to roughly 10 K. The difference and its exact amount depend on the experimental setup, which is a function of the power and wavelength of the incident laser light, sample transparency, etc. We estimate the laser power on the sample to be about 2.5 mW.

The software package Origin 6.0 was used for fitting and curve deconvolution of the spectra.

Results

Figure 2 shows the room temperature Raman (cc) spectra of fayalite, forsterite and tephroite in the wavenumber range between 700 and 1000 cm^{-1} . The two strongest bands at 840 and 816 cm^{-1} in fayalite can be assigned to coupled ν_1 – ν_3 vibrations of the SiO_4 tetrahedra both of A_g symmetry. The higher wavenumber mode of this pair has a stronger ν_1 character and the lower wavenumber one a more ν_3 character (Piriou and McMillan 1983; see also Kolesov and Geiger accompanying article). Both of these modes are notably broadened in fayalite's spectrum, especially that at 840 cm^{-1} ,

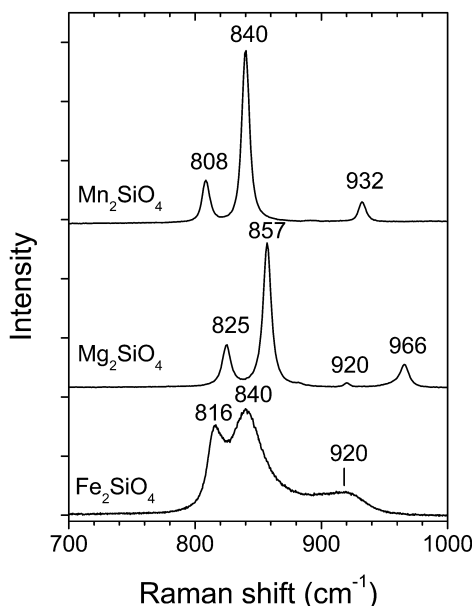


Fig. 2 Raman (*cc*) spectra of tephroite, Mn_2SiO_4 , forsterite, Mg_2SiO_4 , and fayalite, Fe_2SiO_4 , in the wavenumber region of the internal SiO_4 -stretching vibrations at room temperature

where they occur as part of a broad spectral absorption envelope located between 800 and 960 cm^{-1} .

Figure 3 shows the room temperature polarized single-crystal spectrum of fayalite for different symmetries in the same wavenumber range. B_{2g} and B_{3g} modes are observed at 863 and 903 cm^{-1} , respectively, and their line widths (i.e., FWHH) are 8 and 10.5 cm^{-1} . Of the three B_{1g} modes, only that at 827 cm^{-1} (FWHH = 16 cm^{-1}) can be reliably measured, whereas the other two modes have very low

intensities and their estimated positions are approximately 870 and 925 cm^{-1} . Table 1 lists the wavenumbers for the modes of the various symmetries. Chopelas (1991) reports slightly different wavenumbers for the B_{1g} and B_{2g} modes. Figure 4a and b show the high wavenumber region at 5 and 293 K, respectively, with (*cc*) polarization. It can be seen that the strong band at 840 cm^{-1} occurring at 293 K is less intense at 5 K, whereas the band at 827 cm^{-1} is more intense at lower temperatures. Fitting of these envelopes at both temperatures using Lorentzians yields seven bands with peak positions and line widths given in Table 1.

Figure 5 shows the high wavenumber region between 700 and 1000 cm^{-1} and its temperature evolution from 5 to 293 K for (*cc*) polarization. Figure 6 shows the entire spectrum between 100 and 1100 cm^{-1} from 293 to 773 K. Both of these figures exhibit important information. First, the integral intensity of the ν_1 - ν_3 band envelope is lowest around 55 K (Fig. 5). Second, the line width of the band at approximately 840 cm^{-1} decreases slightly with increasing temperature (Fig. 7). In comparison, the line widths of the lattice modes occurring around 200 cm^{-1} increase measurably with increasing temperature, as exemplified by the mode at 172 cm^{-1} (Fig. 7).

Discussion

The spectroscopic observations, combined with an analysis of the fitting results, permit two important conclusions to be made. (1) The wavenumbers of the seven different modes determined from deconvolution of the broad envelope in the (*cc*) spectrum (Fig. 4) and those observed in the polarized spectra (Fig. 3) are

Fig. 3a, b Polarized Raman spectra of fayalite at room temperature

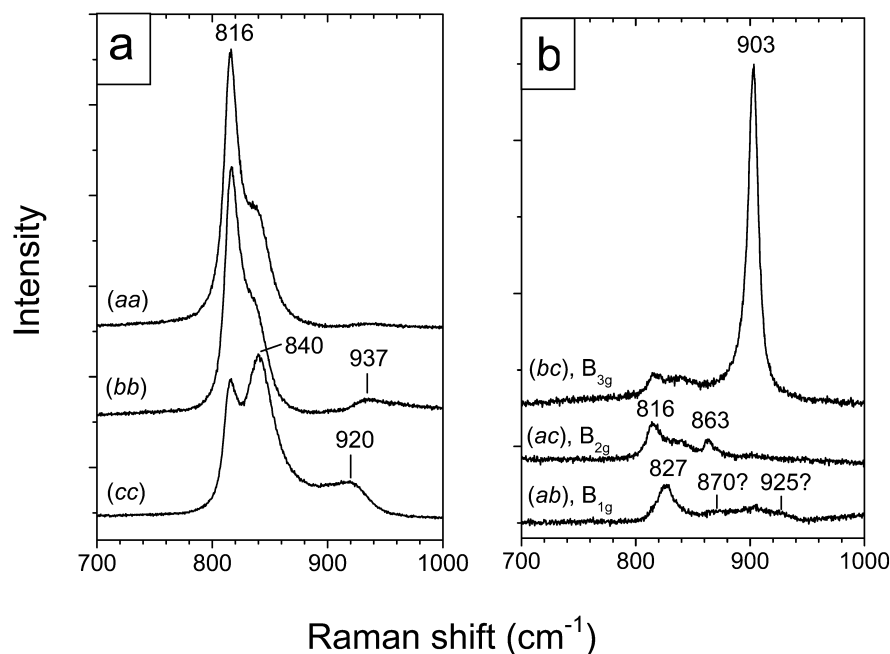
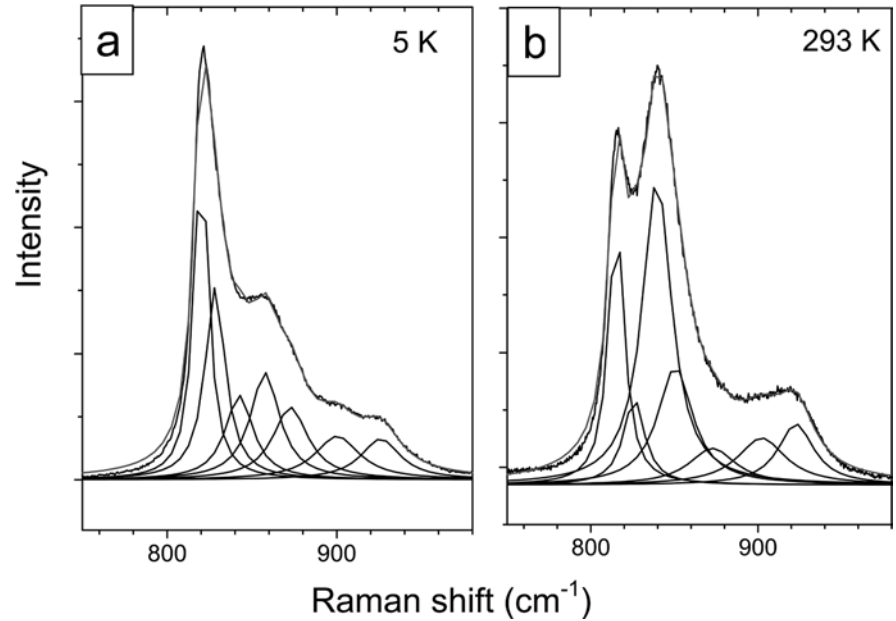


Table 1 Wavenumber (Wn), symmetry (Sym) and FWHH (in cm^{-1}) of the observed SiO_4 modes and results of Lorentz deconvolution of the (cc) spectra at 5 and 293 K

This work		Chopelas (1991)		Lorentz deconvolution			
Wn	Sym	Wn	Sym	5 K		293 K	
				Wn	FWHH	Wn	FWHH
816	A_g	814	A_g	819	10	815	11
827	B_{1g}	822	B_{1g}	826	11	826	15
840	A_g	840	A_g	835	18	840	21
863	B_{2g}	851	B_{1g}	855	29	851	25
870(?)	B_{1g}	860	B_{1g}	871	40	873	34
903	B_{3g}	900	B_{2g}	903	14	902	35
925(?)	B_{3g}	932	A_g	925	34	923	26
937	$A_g(?)$	947	B_{1g}				

Fig. 4a, b Results of curve fitting of the (cc) spectra taken at **a** 5 K and **b**) at 293 K



similar. B_{ig} modes are present in the (cc) spectrum although, because of their symmetry, they should not be. Moreover, all bands are broadened at 5 and 293 K. Both of these effects can result when the selection rules are broken. This could occur, for example, if the SiO_4 -stretching modes combine with excitations of lower energy. The combination of SiO_4 B_{ig} phonon modes, where $i = 1, 2, \text{ or } 3$, with low-energy modes of the same symmetry could allow their observation in the (cc) spectrum, where only totally symmetric modes are “normally” present. (2) The integral intensity of the SiO_4 -mode envelope is a function of temperature and reaches a minimum around 55 K (Fig. 5; the temperature at the laser’s point of incidence on the crystal could be 10 K higher). This is approximately the temperature of the antiferromagnetic transition, $T_N \approx 65$ K (Santoro et al. 1966; Robie et al. 1982). Consequently, the integral intensity of the absorption envelope, consisting of combination modes, is inversely proportional to the degree of magnetic order in fayalite. In other words, the greater the magnetic order, the less intense the combination modes with decreasing temperature from

293 to 55 K. This is obvious for temperatures above T_N , but requires explanation at lower temperatures in order to account for the increase in integral intensity of the absorption envelope with further cooling. The closest alignment between the magnetic spin moments of Fe^{2+} at the M(1) and M(2) sites occurs at approximately $T = T_N$, where the angle of the spin canting at M(1) with respect to the b axis is at a minimum (e.g., 16° at 50 K; Lottermoser et al. 1986; Fuess et al. 1988; Krause et al. 1995). As temperature decreases below T_N , this canting angle increases and the difference in the angle between the directions of the magnetic moments of the Fe^{2+} (1) and Fe^{2+} (2) magnetic sublattices begins to diverge. The integral intensity of the SiO_4 -mode envelope thereby increases below about 55 K.

The observed relationship between the integral intensity of the SiO_4 -mode envelope and magnetic ordering behavior as a function of temperature suggests that the envelope is composed of combination modes consisting of vibrational and magnetic excitations. The vibrations of the oxygen atoms in fayalite could affect the magnetic state of Fe^{2+} in two different ways: (1) by

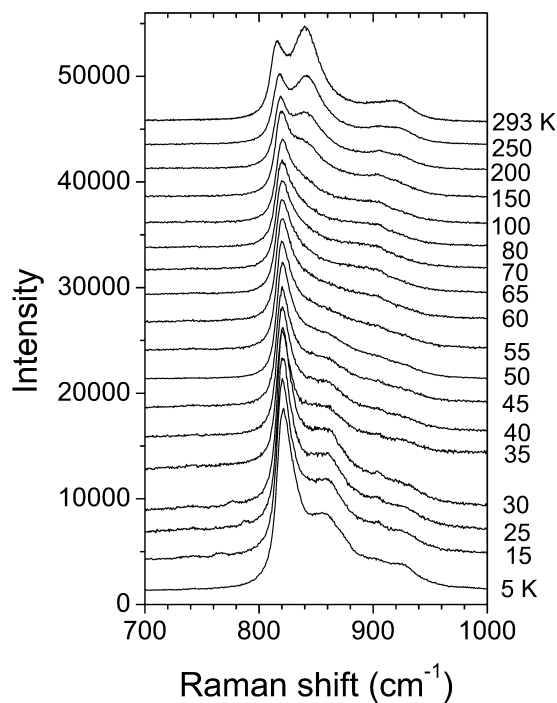


Fig. 5 Temperature evolution of the (cc) spectra between 5 and 293 K

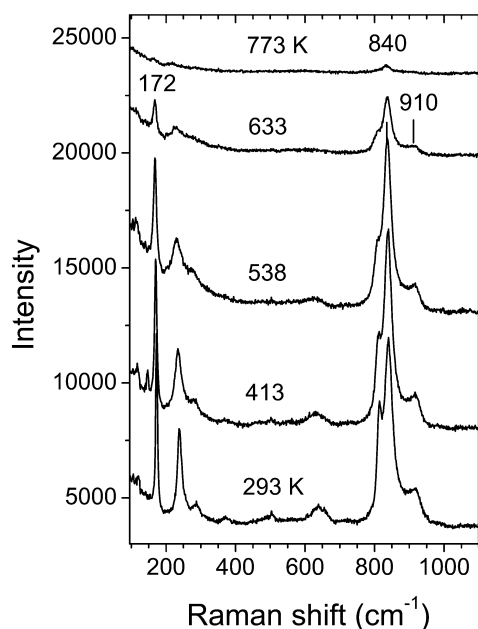


Fig. 6 Temperature evolution of the (cc) spectra between 293 and 773 K

changing the internal single-ion anisotropy that attracts the spin toward some crystallographic direction and (2) through perturbation of the magnetic superexchange energy between neighboring $\text{Fe}^{2+}(1)$ -site and $\text{Fe}^{2+}(2)$ -site spins. The freezing of low-energy lattice vibrations at temperatures below T_N is accompanied by a change in the canting angle of the $\text{Fe}^{2+}(1)$ magnetic

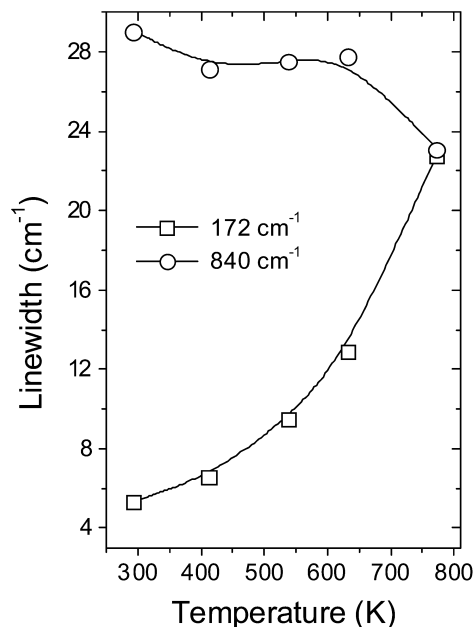


Fig. 7 Line widths of the mode at 840 cm^{-1} and the lattice mode at 172 cm^{-1} as a function of temperature

moment. This confirms the importance of effect (1), which involves displacements of the oxygen atoms that are large enough to change, as well as the Zeeman levels, of Fe^{2+} . Effect (2) is well established (see, for example, Liu et al. 1999, where a strong modulation of an ion-ion exchange interaction through oxygen-related phonons in $\text{Ca}_3\text{Ru}_2\text{O}_7$ occurs). Modulation of the $\text{Fe}^{2+}(1)$ - $\text{Fe}^{2+}(2)$ exchange energy leads to phonon-magnetic excitation coupling. Because only internal SiO_4 modes are broadened, and not low-wavenumber lattice modes having a large Fe^{2+} vibrational character (Fig. 7), one can propose that the main role in the $\text{Fe}^{2+}(1)$ - $\text{Fe}^{2+}(2)$ magnetic interaction occurs via superexchange through the oxygens. The occurrence of coupled phonon-magnetic excitation scattering above the Néel temperature leads us to propose that the low-energy magnetic excitations are short-range and related to so-called incipient magnetism (Hurd 1982). Combination scattering below T_N and a decrease in the interaction at temperatures close to T_N suggest that spin correlation between $\text{Fe}^{2+}(1)$ and $\text{Fe}^{2+}(2)$ produces the observed coupling effects. This is consistent with the conclusion of Ballet et al. (1989) that the $\text{Fe}^{2+}(1)$ - $\text{Fe}^{2+}(1)$ exchange coupling should be weak compared to the $\text{Fe}^{2+}(1)$ - $\text{Fe}^{2+}(2)$ correlation energy. They proposed that the spin direction of $\text{Fe}^{2+}(1)$ is governed by “the competition between their strong single-ion anisotropy favoring a direction near the c axis, and their exchange interaction with the $\text{Fe}^{2+}(2)$ moments attracting them along the b direction”. Oxygen vibrations modulate both of these forces and, thus, should influence the dynamical magnetic ordering. It is necessary to emphasize that the magnetic excitations observed herein are not magnons in the usual sense, that is as quasi-

particles having a long wavelength (or short wave vector) in an ordered system. Schmidt et al. (1992) give the energy of the $\text{Fe}^{2+}(1)\text{--}\text{Fe}^{2+}(2)$ interaction as 140 GHz (4.7 cm^{-1}). The amount of the observed broadening of the SiO_4 -stretching modes is consonant with this value. We propose, therefore, that the magnetic excitations, as manifested in the Raman spectra as combination modes, are short-range with wavelengths on the order of the unit cell or approximately the distance between neighboring Fe^{2+} ions.

The SiO_4 modes remain broadened, but slightly less so up to at least 530 °C, and thus combination scattering exists at the higher temperatures. This is an important observation, because it supports our proposal for the role of magnetic excitations in the scattering process. The general temperature behavior of other modes is an opposite one, whereby their line widths increase with increasing temperature as shown by the low-wavenumber mode at 172 cm^{-1} (Fig. 7). The line width of the band at 840 cm^{-1} decreases slightly above 300 K. This suggests that a decrease in broadening due to weakened magnetic interactions compensates any thermally related broadening. Hofmeister (1987) concluded, based on model phonon-density-of-state heat-capacity calculations largely on phonon spectra measured at room temperature and an analysis of magnetic and electronic effects in fayalite, that complete Fe^{2+} spin disorder is not achieved until temperatures above 700 K.

Implications for thermodynamic behavior

The results of this study have significant implications related to the thermodynamic properties of fayalite and Fe–Mg olivines as well. The macroscopic thermodynamic properties of a phase (e.g., C_p and S) derive from its lattice-dynamic behavior, as shown in Raman spectra, for instance. Numerous crystal-chemical type models have been presented in the mineralogical literature over the years to estimate, for example, third-law entropies of silicates using macroscopic volume-entropy systematics of component oxides (e.g., Wood 1981). All of these models have difficulties in estimating the heat capacities and entropies for many transition-metal-containing silicates. This is especially true for the case of fayalite, whose entropy estimates have proved problematic. Modifications to the models to include electronic effects such as crystal-field stabilization energies for Fe^{2+} (Wood 1981) do not resolve the difficulties. In many cases the problem may lie in accounting for differences in the low-temperature magnetic properties between the component oxides and the phase whose entropy is to be calculated. For example, fayalite has a large heat effect associated with its magnetic phase transition at $\sim 65\text{ K}$, while the magnetic phase transition for ‘FeO’ lies at a much higher temperature around 190 K (see Grønvold et al. 1993 for a detailed discussion of the C_p behavior of

wüstite). The magnetic properties of a phase can be reflected further in the lattice dynamic behavior as in fayalite. Simple macroscopic- and static-based crystal-chemical models cannot give quantitatively the lattice dynamic (i.e., thermodynamic) properties of some transition-metal-containing phases, because they cannot account for subtle, yet important, effects such as magnetic energies and magnetic–phonon interactions. These properties are strongly dependent on the structure and sites in which the magnetic cations occur and are not “transferable” from phase to phase. It cannot be expected that such modeling can give accurate estimates for the third-law entropy for some transition-metal-bearing silicates.

The effect of magnetic behavior on the thermodynamic properties of many important Fe silicates, and also Fe–Mg solid solutions, is not well understood. More low-temperature C_p and vibrational spectroscopic measurements on Fe–Mg silicates are critically needed to make progress in this area.

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