

# Infrared properties of ferropericlase $\text{Mg}_{1-x}\text{Fe}_x\text{O}$ : Experiment and theory

Tao Sun,<sup>1,\*</sup> Philip B. Allen,<sup>1</sup> David G. Stahnke,<sup>2</sup> Steven D. Jacobsen,<sup>3</sup> and Christopher C. Homes<sup>4</sup>

<sup>1</sup>*Department of Physics and Astronomy, State University of New York, Stony Brook, New York 11794, USA*

<sup>2</sup>*Department of Physics, University of California, San Diego, La Jolla, California 92093, USA*

<sup>3</sup>*Department of Earth and Planetary Sciences, Northwestern University, Evanston, Illinois 60208, USA*

<sup>4</sup>*Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory, Upton, New York 11973, USA*

(Received 19 April 2007; revised manuscript received 15 January 2008; published 4 April 2008)

The temperature dependence of the reflectance spectra of magnesium oxide (MgO) and ferropericlase ( $\text{Mg}_{1-x}\text{Fe}_x\text{O}$ , for  $x=0.06$  and  $x=0.27$ ) have been measured over a wide frequency range ( $\approx 50\text{--}32\,000\text{ cm}^{-1}$ ) at 295 and 6 K. The complex dielectric function has been determined from a Kramers-Kronig analysis of the reflectance. The spectra of the doped materials resemble pure MgO in the infrared region, but with much broader resonances. We use a shell model to calculate the dielectric function of ferropericlase, including both anharmonic phonon-phonon interactions and disorder scattering. These data are useful in understanding the vibrational properties of ferropericlase.

DOI: [10.1103/PhysRevB.77.134303](https://doi.org/10.1103/PhysRevB.77.134303)

PACS number(s): 63.20.K-, 63.20.kp, 74.25.Kc, 78.30.-j

## I. INTRODUCTION

Ferropericlase ( $\text{Mg}_{1-x}\text{Fe}_x\text{O}$ , with  $x=0.10\text{--}0.15$ ), is thought to be one of the major constituents of the Earth's lower mantle (660–2900 km depth).<sup>1</sup> The name “magnesiowüstite” is also used, but properly refers to the doping region  $x$  close to the wüstite ( $x=1$ ), rather than the periclase ( $x=0$ ) limit. A detailed knowledge of the physical properties (elasticity, electronic and vibrational excitations, etc.) of ferropericlase is meaningful for geophysical research. In contrast with periclase (pure MgO), which is a typical ionic insulator with a band gap of 7.8 eV,<sup>2</sup> ferropericlase has crystal field levels and charge transfer bands at much lower energies due to the presence of  $\text{Fe}^{2+}$ . These electronic excitations have been studied by measuring the optical absorption spectra in the frequency range of about 2000 to 25 000  $\text{cm}^{-1}$ .<sup>3,4</sup> The presence of  $\text{Fe}^{2+}$  also influences the vibrational excitations of the system. With strong disorder scattering of propagating vibrational states, the harmonic eigenstates of the disordered crystal do not necessarily have a well-defined wave number, and may not propagate ballistically. One way to study the vibrational excitations is by doing infrared (IR) reflectance spectroscopy. To our knowledge, such a study for  $\text{Mg}_{1-x}\text{Fe}_x\text{O}$  with  $x < 0.4$  has not been carried out yet.

In pure MgO, the anharmonic phonon-phonon interactions causes a shoulder at  $\sim 640\text{ cm}^{-1}$  in the IR reflectance spectrum.<sup>5</sup> Thus anharmonicity should also be included in analyzing the infrared reflectance of ferropericlase. It is an interesting physics problem to understand the vibrational properties of such a disordered anharmonic crystal.

In this paper we report the temperature-dependent infrared reflectance measurements of magnesium oxide and ferropericlase for several Fe concentrations at ambient pressure. We construct a model in which anharmonic phonon-phonon interactions and disorder scattering are treated separately. Their effects are then combined for comparison with the experimental data.

## II. EXPERIMENTAL MEASUREMENTS

Our samples are homogeneously doped single crystals, in which  $\text{Fe}^{3+}/\Sigma\text{Fe} \approx 0.02$  for the 6% sample and 0.05 for the

27% sample. In our analysis, the influence of  $\text{Fe}^{3+}$  and magnesium vacancies is ignored. A detailed description of the samples' synthesis, crystallography, and elastic properties is in Ref. 6. The samples are rectangular slabs with typical dimensions of 1 mm  $\times$  2 mm, with a thickness of  $\approx 0.3$  mm. In order to reduce interference effects due to reflections from the back surface, the samples have been wedged. However, due to the thin nature of the samples, the largest wedge that could be introduced was  $\approx 15^\circ$ . The reflectance spectra has been measured at a near-normal angle of incidence at 295 and 6 K over a wide frequency range from  $\approx 50$  to about 32 000  $\text{cm}^{-1}$  on Bruker IFS 66v/S and 113v spectrometers using an *in situ* evaporation technique.<sup>7</sup> Figure 1(a) shows the measured reflectance at 6 K in the whole frequency range. Figure 1(b)–1(d) show the measured reflectance from 0–1000  $\text{cm}^{-1}$  at 295 and 6 K of pure MgO, and  $\text{Mg}_{1-x}\text{Fe}_x\text{O}$ , for  $x=0.06$  and 0.27, respectively. Although wedging the samples has been very effective at reducing interference effects, weak fringes may still be detected at low temperature below about 150  $\text{cm}^{-1}$ . The complex dielectric function  $\epsilon = \epsilon_1 + i\epsilon_2$  has been determined from a Kramers-Kronig analysis of the reflectance, where extrapolations are supplied for  $\omega \rightarrow 0, \infty$ . At low frequency, an insulating response is assumed and  $R(\omega \rightarrow 0) \approx 0.27, 0.28$ , and 0.31 for MgO, and the 6 and 27 % Fe-doped materials, respectively. Above the highest measured frequency the reflectance has been assumed to be constant to approximately 75 000  $\text{cm}^{-1}$ , above which a free-electron approximation has been assumed ( $R \propto 1/\omega^4$ ). The imaginary part of the resulting dielectric functions at 6 and 295 K of pure MgO, and  $\text{Mg}_{1-x}\text{Fe}_x\text{O}$ , for  $x=0.06$  and  $x=0.27$ , are shown in Figs. 1(e)–1(g), respectively. They contain most of the physical information, and are the focus of our theoretical analysis. The optical features have been fit to a classical oscillator model using the complex dielectric function

$$\epsilon(\omega) = \epsilon_\infty + \sum_j \frac{\omega_{p,j}^2}{\omega_{\text{TO},j}^2 - \omega^2 - i2\omega\gamma_j}, \quad (1)$$

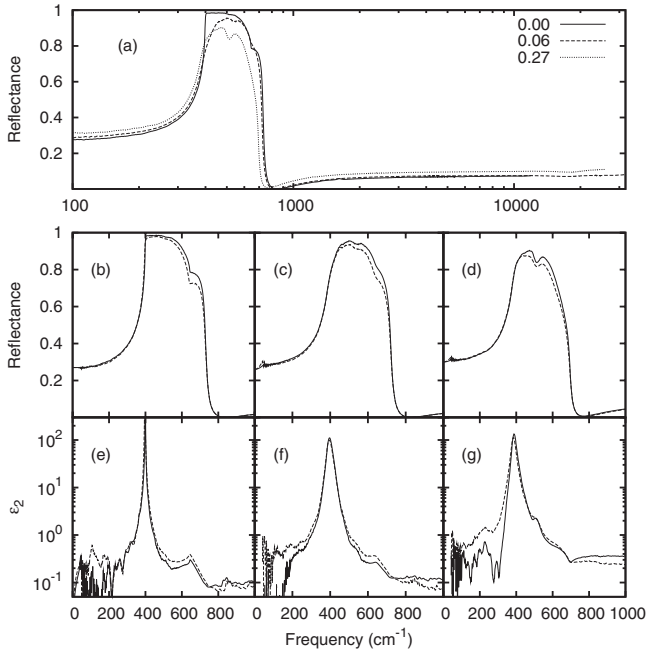


FIG. 1. The measured reflectance  $R(\omega)$  (a) in the whole frequency range at 6 K. The solid, dashed, and dotted lines correspond to pure MgO,  $\text{Mg}_{1-x}\text{Fe}_x\text{O}$  for 6 and 27 % Fe doping, respectively. Parts below  $1000 \text{ cm}^{-1}$  are shown in (b) pure MgO, and  $\text{Mg}_{1-x}\text{Fe}_x\text{O}$  for (c) 6% and (d) 27% Fe doping. The corresponding imaginary part of the dielectric functions  $\epsilon_2(\omega)$ . (e) pure MgO, and  $\text{Mg}_{1-x}\text{Fe}_x\text{O}$  for (f) 6% and (g) 27% Fe doping. The solid line corresponds to data measured at 6 K, dashed line corresponds to data at 295 K.

where  $\epsilon_\infty$  is a high-frequency contribution and  $\omega_{\text{TO},j}$ ,  $2\gamma_j$ , and  $\omega_{p,j}$  are the frequency, full width, and effective plasma frequency (strength) of the  $j$ th vibration. The results of nonlinear least-squares fits to the reflectance and  $\epsilon_2(\omega)$  are shown in Table I. In addition to the strong feature in  $\epsilon_2(\omega)$  seen at about  $400 \text{ cm}^{-1}$ , other features at  $\approx 520$  and  $640 \text{ cm}^{-1}$  are also clearly visible in  $\epsilon_2(\omega)$  shown in Fig. 1; however, these features are very weak and as a result the strengths and widths of these modes are difficult to determine reliably.

TABLE I. A comparison of the fitted values of the static and high-frequency contributions to the real part of the dielectric function at room temperature, as well as the fitted frequency, full width, and effective plasma frequency ( $\omega_{\text{TO}}$ ,  $2\gamma$ , and  $\omega_p$ , respectively) of the feature associated with the strong TO mode in MgO, and the 6 and 27 % Fe-doped materials at 295 and 6 K. The units of  $\omega_{\text{TO}}$ ,  $2\gamma$ , and  $\omega_p$  are in  $\text{cm}^{-1}$ . The strength of the TO mode is also expressed as a dimensionless oscillator strength  $S = \omega_p^2 / \omega_{\text{TO}}^2$ . Values of  $\epsilon_0$  and  $\epsilon_\infty$  are at 295 K. Their estimated uncertainties are about  $\pm 0.1$ . The uncertainty in  $\omega_{\text{TO}}$  is  $\pm 0.1 \text{ cm}^{-1}$ . The uncertainties for  $2\gamma$  are  $\pm 0.1 \text{ cm}^{-1}$  in the pure material, and  $\pm 0.5 \text{ cm}^{-1}$  in the Fe-doped materials. The uncertainty in  $\omega_p$  is  $\pm 20 \text{ cm}^{-1}$ .

$\text{Mg}_{1-x}\text{Fe}_x\text{O}$	$\epsilon_0$	$\epsilon_\infty$	295 K			6 K		
			$\omega_{\text{TO}}$	$2\gamma$	$\omega_p$ (S)	$\omega_{\text{TO}}$	$2\gamma$	$\omega_p$ (S)
pure	9.2	2.95	396.5	3.44	1010 (6.5)	398.9	1.72	1030 (6.7)
$x=0.06$	10.8	3.10	395.6	30.5	1090 (7.6)	396.7	29.1	1120 (8.0)
$x=0.27$	11.8	3.65	384.5	28.6	1100 (8.2)	388.6	25.7	1140 (8.6)

### III. COMPUTATIONAL METHODS

#### A. General scheme

Infrared dielectric properties of ionic crystals are contained in the linear response function  $\epsilon_{\alpha\beta}(\omega) = \epsilon_{\alpha\beta}(\infty) + 4\pi\chi_{\alpha\beta}(\omega)$ .<sup>8</sup> Considering only the first-order moment of the electric dipole, the dielectric susceptibility of a crystal can be related to its displacement-displacement retarded Green's function by

$$\chi_{\alpha\beta}(\omega) = -\frac{1}{NV} \sum_c \sum_{ls\gamma} Z_{\alpha\gamma}(ls) Z_{\beta\delta}(l's') G_{\gamma\delta}(ls, l's'; \omega), \quad (2)$$

where  $Z_{\alpha\beta}(ls)$  is the Born effective charge tensor of the atom  $s$  at site  $l$ . The volume of a single cell is  $V_c$ , and  $N$  is the number of the cells in the whole crystal. The Green's function  $G_{\alpha\beta}(ls, l's'; \omega)$  can be evaluated from its equation of motion.<sup>9</sup> For a harmonic material, the vibrational Hamiltonian is quadratic and can be solved exactly. We denote the eigenvectors of a pure crystal as  $1/\sqrt{N} \hat{e}_\alpha(s|\mathbf{q}j) e^{i\mathbf{q}\cdot\mathbf{R}(ls)}$ , the corresponding eigenvalues as  $\omega_{\mathbf{q}j}$ , those of a disordered crystal as  $e_\alpha(s|j)$  and  $\omega_j$ , the Green's function of the pure as  $\mathbf{g}$ , and the disordered as  $\mathbf{G}^0$ . Then

$$g_{\alpha\beta}(ls, l's'; \omega) = \sum_{\mathbf{q}j} \frac{\hat{e}_\alpha(s|\mathbf{q}j) \hat{e}_\beta^*(s'|\mathbf{q}j) e^{i\mathbf{q}\cdot[\mathbf{R}(ls) - \mathbf{R}(l's')]} }{N \sqrt{M(s)M(s')} (\omega^2 - \omega_{\mathbf{q}j}^2 + i2\omega\eta)}, \quad (3)$$

$$G_{\alpha\beta}^0(ls, l's'; \omega) = \sum_j \frac{e_\alpha(s|j) e_\beta^*(s'|j)}{\sqrt{M(ls)M(l's')} (\omega^2 - \omega_j^2 + i2\omega\eta)}, \quad (4)$$

where the mass of the atom  $s$  is denoted as  $M(s)$  in the pure crystal,  $M(ls)$  in the disordered crystal, with the extra label  $l$  to specify its site, and  $\eta$  is an infinitesimal number ensuring causality.

Anharmonic interaction will couple these modes and make exact solution impossible. The standard treatment of

this many-body effect uses the Dyson equation to define a self-energy for each mode. We can either choose  $e_\alpha(s|j)$  as the unperturbed states, then the only interaction will be anharmonicity, or choose  $1/\sqrt{N}\hat{e}_\alpha(s|\mathbf{q}j)e^{i\mathbf{q}\cdot\mathbf{R}(ls)}$  as the basis and treat disorder as an extra perturbation. The first approach has

been used by one of the authors to study the anharmonic decay of vibrational states in amorphous silicon.<sup>10</sup> In this paper we use a hybrid approach. We write the dielectric function of a disordered anharmonic crystal in the perfect crystal harmonic basis as

$$\epsilon_{\alpha\beta}(\omega) = \epsilon_{\alpha\beta}(\infty) + \frac{4\pi}{V_c} \sum_{j=1}^{\text{TO}} \frac{\sum_{s\gamma} Z_{\alpha\gamma}(s) \frac{\hat{e}_\gamma(s|0j)}{\sqrt{M(s)}} \sum_{s'\delta} Z_{\beta\delta}(s') \frac{\hat{e}_\delta^*(s'|0j)}{\sqrt{M(s')}}}{\{\omega(0j)^2 - \omega^2 + 2\omega(0j)[\Delta(0j, \omega) - i\Gamma(0j, \omega)]\}}, \quad (5)$$

where  $\omega(0j) \equiv \omega_{\text{TO},j}$  is the frequency at  $\mathbf{q}=0$  of the  $j$ th TO branch. The terms  $\Delta(0j, \omega)$  and  $\Gamma(0j, \omega)$  correspond to the real and imaginary part of the mode's self-energy  $\Sigma(0j, \omega)$ . Then we split this self-energy into two parts:  $\Sigma = \Sigma_{\text{anhar}} + \Sigma_{\text{disorder}}$ . Each piece is calculated independently. This is equivalent to omitting all the diagrams where the disorder scattering vertex appears inside an anharmonic interaction loop. The anharmonic interaction of ferropericlate is assumed to be the same as that of pure MgO, i.e., the influence of disorder on anharmonic coefficients is totally ignored. Disorder is treated by exact diagonalization without anharmonicity, it is then converted to a self-energy of the TO mode in the perfect crystal harmonic basis. These approximations are tested by comparing with the experimental results.

### B. Shell model

The scheme described above is general. It does not depend on which microscopic model is chosen to get harmonic phonons, disorder scattering strength, and higher-order force constants. Here we use an anharmonic shell model, with shell parameters fitted to experiments. The harmonic phonon properties in this paper are calculated with the general utility lattice program (GULP) code.<sup>11</sup>

Two sets of shell parameters<sup>11,12</sup> are used for MgO: *S*-I and *B*, and one for FeO: *S*-II. *S*-I and *S*-II are rigid shell models in which  $\text{O}^{2-}$  has the same set of parameters, thus they can be conveniently used to simulate ferropericlate. *B* is an isotropic breathing shell model which gives better fit to the experimental data. However, it cannot be directly used for ferropericlate. For FeO the elastic constants  $C_{12} > C_{44}$ , while the isotropic breathing shell model is only suitable for cases where  $C_{12} < C_{44}$ .<sup>13</sup> We treat *B* as a reference to check our anharmonic calculations based on *S*-I. All the model parameters are listed in Table II. Table III contains the calculated physical properties and corresponding experimental values. Phonon dispersion curves for the pure crystals of MgO and FeO are shown in Fig. 2.

### C. Anharmonicity

A complete calculation of anharmonicity is tedious, even for a pure crystal.<sup>8</sup> Thus we ignore the less important terms

and focus on the dominant one. From Eq. (5) it is clear that since  $|\Sigma| = |\Delta - i\Gamma|$  is small compared to  $\omega_{\text{TO}}$ , the real part of the self-energy  $\Delta$  has negligible influence on  $\epsilon_2(\omega)$ , except to shift its resonant frequency. The shell models we use are fitted to the experimental data measured at room temperature. The anharmonic shift is small, compared with the shift caused by disorder scattering. Thus, we ignore it completely and only consider the imaginary part of the self-energy

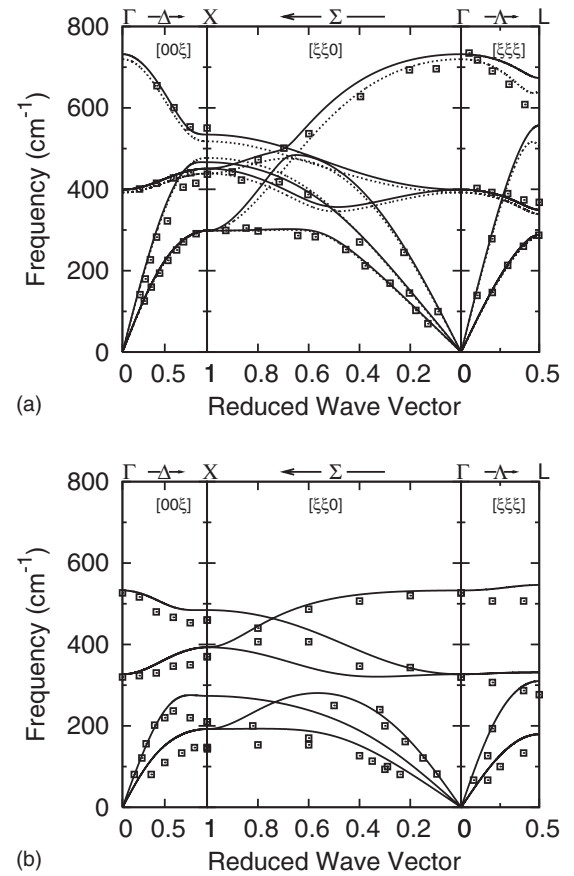


FIG. 2. Phonon dispersions of the pure crystals. (a) MgO, solid line corresponds to the rigid-shell model *S*-I, dashed line to the isotropic breathing-shell model *B*, dots are the experimental data taken from Ref. 14; (b) FeO, solid line corresponds to the rigid-shell model *S*-II, dots are the experimental data taken from Ref. 15.

$\Gamma_{\text{anharm}}(0j, \omega)$ . To the lowest order  $\Gamma_{\text{anharm}}(0j, \omega)$  can be written as<sup>8,17</sup>

$$\Gamma_{\text{anharm}}(0j, \omega) = \frac{18\pi}{\hbar^2} \sum_{\mathbf{q}_{j_1 j_2}} \left| V \begin{pmatrix} 0 & \mathbf{q} & -\mathbf{q} \\ j & j_1 & j_2 \end{pmatrix} \right|^2 \{ (n_1 + n_2 + 1) \times [\delta(\omega_1 + \omega_2 - \omega) - \delta(\omega_1 + \omega_2 + \omega)] + (n_2 - n_1) [\delta(\omega_2 - \omega_1 + \omega) - \delta(\omega_1 - \omega_2 + \omega)] \}, \quad (6)$$

where  $n_1 = n(\mathbf{q}_{j_1})$  is the Bose-Einstein population factor of the mode, and  $\omega_1 = \omega(\mathbf{q}_{j_1})$  is the corresponding frequency. The anharmonic coefficient  $V \begin{pmatrix} 0 & \mathbf{q} & -\mathbf{q} \\ j & j_1 & j_2 \end{pmatrix}$  is computed from the nearest-neighbor third-order force constants using standard formulas.<sup>8,17–19</sup> Other parameters (Born effective charge tensors and harmonic eigenvectors) are obtained from GULP. The integration over  $q$  space is done with the tetrahedron method, using 1/48 of the Brillouin zone, and averaging over  $x$ ,  $y$ , and  $z$  polarizations. We use 3345  $q$  points, equivalent to 160 560  $q$  points in the whole Brillouin zone.

#### D. Disorder scattering

The self-energy of a vibrational mode caused by disorder scattering is defined statistically,<sup>9,20</sup>

$$\langle\langle \mathbf{G}^0 \rangle\rangle = \mathbf{g} + \mathbf{g} \Sigma \langle\langle \mathbf{G}^0 \rangle\rangle,$$

where  $\langle\langle \mathbf{G}^0 \rangle\rangle$  denotes the Green's function averaged over different impurity distributions. We slightly modify this definition by including the Born effective charge. From Eqs. (3) and (4), we define the following equation:

TABLE II. Shell model parameters used in the calculation. They are taken from Refs. 11 and 12. The short-range repulsive potential is assumed to be a two-body Buckingham type: for S-I and S-II,  $V(r) = A \exp(-r/\rho) - C/r^6$ ; for B,  $V(r) = A \exp[-(r-r_0)/\rho] - C/r^6$ . The parameter  $k$  represents the spring constant between core and shell. Rows in which atomic symbols have a star (\*) are for the B model. The label “shell” denotes a potential that acts on the central position of the shell, while “bshell” denotes an interaction that acts on the radius of the shell which was fixed at 1.2 Å. An extra parameter in B model is  $k_{\text{BSM}} = 351.439 \text{ eV Å}^{-2}$ . The equilibrium shell radius  $r_0$  is 1.1315 Å after optimization.

	$Z_{\text{core}} (e)$	$Z_{\text{shell}} (e)$	$k (\text{eV})$
O	0.9345	-2.9345	51.712
Mg	2		
Fe	-1.1682	3.1682	69.562
O*	0.8	-2.8	46.1524
Mg*	2		
	$A (\text{eV})$	$\rho (\text{Å})$	$C (\text{eV Å}^6)$
O shell-O shell	22764.3	0.149	20.37
Mg core-O shell	1346.6	0.2984	0.0
Fe shell-O shell	1231.2	0.3086	0.0
O* shell-O* shell	0.0	0.3	54.038
Mg* core-O* bshell	28.7374	0.3092	0.0

$$\begin{aligned} & \langle\langle \sum_{\gamma} \sum_{\delta} Z_{\alpha\gamma}(ls) G_{\gamma\delta}^0(ls, l's'; \omega) Z_{\delta\beta}(l's') \rangle\rangle \\ &= \sum_{\gamma} \sum_{\delta} Z_{\alpha\gamma}(s) \tilde{g}_{\gamma\delta}(ls, l's'; \omega) Z_{\delta\beta}(s'), \end{aligned} \quad (7)$$

where

$$\tilde{g}_{\gamma\delta}(ls, l's'; \omega) = \sum_{\mathbf{q}j} \frac{\hat{e}_{\gamma}(s|\mathbf{q}j) \hat{e}_{\delta}^*(s'|\mathbf{q}j) e^{i\mathbf{q} \cdot [\mathbf{R}(ls) - \mathbf{R}(l's')]} }{N \sqrt{M(s)M(s')} [\omega^2 - \omega_{\mathbf{q}j}^2 - 2\omega_{\mathbf{q}j} \Sigma_{\text{disorder}}(\mathbf{q}j, \omega)]}. \quad (8)$$

The self-energy defined in this way guarantees that the dielectric susceptibilities calculated from  $\mathbf{G}^0$  and  $\tilde{\mathbf{g}}$  are the same. Summing over all sites of the crystal leaves only TO modes on the right-hand side of Eq. (7). Thus, once we get the averaged dielectric susceptibility  $\langle\langle \chi_{\alpha\beta} \rangle\rangle$  from the exact eigenvectors of the disordered crystal, we can extract the self-energy of its TO phonon.

We expand an orthogonal eight-atom MgO unit cell in each direction by 5 times, which gives a  $5 \times 5 \times 5$  supercell containing 1000 atoms. Then we randomly replace the corresponding number of  $\text{Mg}^{2+}$  by  $\text{Fe}^{2+}$ . The shell parameters of  $\text{Mg}^{2+}$  are from the S-I model, those of  $\text{Fe}^{2+}$  are from S-II model, those of  $\text{O}^{2-}$  are the same in both models. From Eqs. (2) and (4), for each configuration we have a harmonic susceptibility

$$\chi_{\alpha\beta}(\omega) = \frac{1}{NV_c} \sum_{j=1}^{\text{modes}} \frac{\sum_{ls\gamma} Z_{\alpha\gamma}(ls) \frac{e_{\gamma}(ls|j)}{\sqrt{M(ls)}} \sum_{l's'\delta} Z_{\beta\delta}(l's') \frac{e_{\delta}^*(l's'|j)}{\sqrt{M(l's')}}}{\omega_j^2 - \omega^2 - i2\omega\eta}. \quad (9)$$

We can choose a small value for  $\eta$  and evaluate Eq. (9) directly (Lorentzian broadening). However, insofar as  $\eta$  is finite, it is equivalent to have each mode  $j$  in Eq. (9) an

imaginary self-energy (lifetime) linear in frequency  $\omega$ . The self-energy of the TO phonon  $\Sigma_{\text{disorder}}$  extracted from this approach will depend on frequency linearly. Replacing the



factor  $2\omega$  by  $2\omega_j$  will not help either, as each mode  $j$  now has a lifetime independent of frequency, and  $\Sigma_{\text{disorder}}$  will be a constant depending on  $\eta$  when  $\omega \rightarrow 0$ . To avoid such artifacts we use

$$\frac{1}{\omega_j^2 - \omega^2 - i2\omega\eta} = \frac{1}{\omega_j^2 - \omega^2} + \frac{i\pi}{2\omega} [\delta(\omega - \omega_j) + \delta(\omega + \omega_j)]$$

to separate the real ( $\chi_1$ ) and imaginary part ( $\chi_2$ ) of the dielectric susceptibility. Then we divide the vibrational spectrum into equally sized bins ( $1 \text{ cm}^{-1}$ ) and compute  $\chi_2$  as a histogram. The real part  $\chi_1$  is obtained from  $\chi_2$  from the Kramers-Kronig relation. Many such supercells are built and their  $\epsilon_\infty$  and  $\chi$  calculated. We find that ten configurations are sufficient to give a well converged average. The final  $\epsilon_\infty$  and  $\chi$  are assumed to be the averaged values of all configurations. To remove the unphysical spikes caused by the finite size of our supercells, while keeping the main features unchanged, we further smooth the dielectric susceptibility by averaging over adjacent bins iteratively,

$$\chi_2^{n+1}(j) = \frac{1}{6} [\chi_2^n(j-1) + 4\chi_2^n(j) + \chi_2^n(j+1)]. \quad (10)$$

In this way we successfully simulate the dielectric function of a “real” crystal (real in the sense that except for finite size, disorder scattering is treated without any further approximations). These results, together with anharmonicity, are summarized in the next section.

#### IV. COMPARISONS AND DISCUSSION

The anharmonic effects in pure MgO are shown in Fig. 3. The computational results and experimental values are quite close, especially near  $640 \text{ cm}^{-1}$  which corresponds to TO + TA combination mode. Below  $800 \text{ cm}^{-1}$ , the rigid shell model *S-I* and breathing shell model *B* give almost identical self-energies. The discrepancy in the high-frequency range indicates that the dispersion relations from empirical models are less accurate for high-frequency optical branches. The width of TO mode at the reststrahlen frequency  $\omega_{\text{TO}}$  is less accurate, as  $\Gamma_{\text{anharmon}}(0j, \omega)$  is small in the region  $\omega \approx \omega_{\text{TO}}$  and higher-order anharmonic effects become important.<sup>21</sup>

Figures 4 and 5 show how anharmonicity and disorder scattering influence the dielectric function. For the 6% sample it is clear that the shoulder near  $640 \text{ cm}^{-1}$  is caused by anharmonicity, while the shoulder at about  $520 \text{ cm}^{-1}$  is

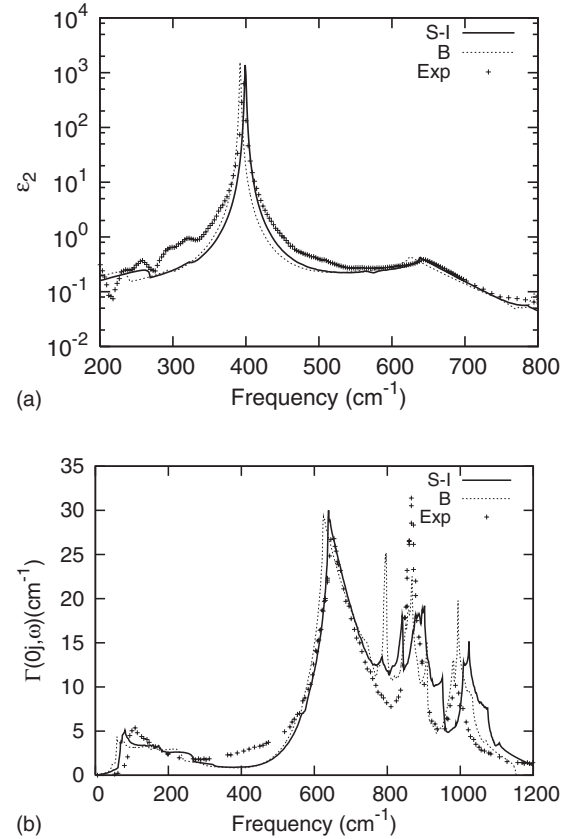


FIG. 3. Computed anharmonic properties compared with experimental data for pure MgO. (a) The imaginary part of dielectric function at 295 K; the experimental data are the same as those in Fig. 1(e). (b) The imaginary part of self-energy at 295 K; the experimental data are digitized from Ref. 22, which are fit to infrared spectra based on a semiquantum dielectric function model.

due to disorder scattering. Disorder scattering becomes stronger for the 27% sample and seems to contribute to all the shoulders. The shoulder caused by anharmonicity corresponds to a peak in the two-phonon DOS, while shoulders caused by disorder scattering are related to peaks in the one-phonon DOS.

Figure 6 contains the reflectance computed from the dielectric functions at 295 and 6 K shown in Figs. 4 and 5. As in the case of pure MgO, the agreement between theory and experiment is better in the region where the self-energy caused by lowest-order perturbation is large. Near the reststrahlen frequency  $\omega_{\text{TO}}$ , the self-energy is smaller, and  $R(\omega)$

TABLE III. Physical properties of pure MgO and FeO, compared with shell model results.

	$a$ (Å)	$C_{11}$ (GPa)	$C_{12}$ (GPa)	$C_{44}$ (GPa)	$\epsilon_0$	$\epsilon_\infty$	TO ( $\text{cm}^{-1}$ )
MgO (expt. <sup>a</sup> )	4.212	297.0	95.2	155.7	9.86	2.96	401
<i>S-I</i>	4.225	370.9	163.0	163.0	9.88	2.94	399
<i>B</i>	4.212	297.0	95.0	155.7	9.89	2.94	392
FeO (expt. <sup>b</sup> )	4.310	359	156	56	14.2	5.4	320
<i>S-II</i>	4.324	327	149	149	14.18	5.34	327

<sup>a</sup>References 11, 12, and 16.

<sup>b</sup>Reference 16.

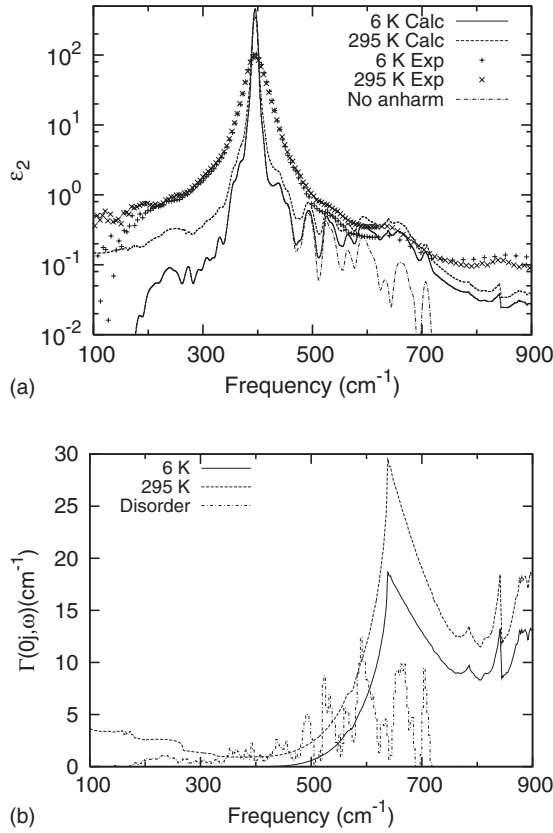


FIG. 4. The anharmonic and disordering scattering effects in  $\text{Mg}_{1-x}\text{Fe}_x\text{O}$  for the 6% Fe-doped sample. (a) Imaginary part of the dielectric function. The labels “6 K Calc” and “295 K Calc” denote the calculated curves, including both disorder scattering and anharmonic interactions at the corresponding temperature. Experimental data are the same as those in Fig. 1(f). The label “No anhar” denotes the dielectric function calculated from disorder scattering only. (b) Imaginary part of self-energy. The labels “6 K” and “295 K” denote the self-energies caused by anharmonic interaction at the corresponding temperature; “disorder” denotes the self-energy due to disorder scattering, which is computed by histogram method where the bin size equals  $1 \text{ cm}^{-1}$ , then iteratively averaged 30 times. The total self-energies are the sum of these two pieces, and are used in calculating the “6 K Calc” and “295 K Calc” dielectric functions shown in (a).

is more sensitive to details. Our model underestimates the broadening of the resonance, but correctly identifies the sources of broadening.

It is of interest to determine whether the disorder scattering is mainly due to the differences in mass or in the interatomic potential. Thus we repeat the above procedure with a model which only contains mass disorder, i.e., Fe is treated as an isotope of Mg, its shell parameters are the same as  $\text{Mg}^{2+}$  in the *S-I* model. It turns out the most significant factor is  $\epsilon_\infty$ . For the isotope model (*S-I*)  $\epsilon_\infty$  is the same as pure MgO (2.94), for the *S-II* model  $\epsilon_\infty$  increases to 3.05 for 6% Fe and 3.47 for 27%, in reasonable agreement with the results shown in Table I. The LO frequency predicted from the isotope model is larger than the experimental value. The differences in the interatomic potentials change the relative strength of the self-energy, but in both cases the self-energy

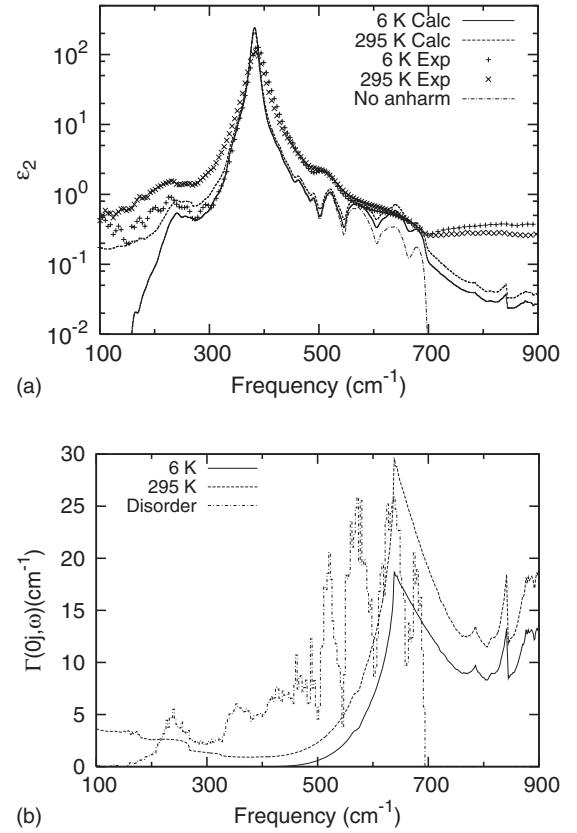


FIG. 5. The anharmonic and disordering scattering effects in  $\text{Mg}_{1-x}\text{Fe}_x\text{O}$  for the 27% Fe-doped sample. (a) Imaginary part of the dielectric function; (b) imaginary part of self-energy. The computation procedure is the same as for the 6% Fe doping.

spectra carry features of the one phonon DOS of pure MgO.

In addition to phonons, electronic transitions may also influence the infrared dielectric properties of ferropericlas. Wong<sup>23</sup> measured the far-infrared absorption spectra of iron-doped MgO. A line at  $105 \text{ cm}^{-1}$  was observed with a peak absorption coefficient of  $1.5 \text{ cm}^{-1}$  and a width of  $\approx 9 \text{ cm}^{-1}$  at 20 K in a sample with 0.2% Fe. This feature is attributed to the transition  $\Gamma_{5g} \rightarrow \Gamma_{3g}, \Gamma_{4g}$  of  $\text{MgO:Fe}^{2+}$  at cubic sites. If we assume the absorption coefficient is proportional to the impurity concentration, then we can estimate the corresponding  $\epsilon_2$  at  $105 \text{ cm}^{-1}$  by  $\epsilon_2(\omega) = \frac{n\alpha(\omega)}{2\pi\omega}$ , where  $n$  is the refractive index (for pure MgO,  $n \approx 3.2$  at  $105 \text{ cm}^{-1}$ ),  $\alpha(\omega)$  is the absorption coefficient at frequency  $\omega$  (in units of  $\text{cm}^{-1}$ ). The value of  $\epsilon_2$  is about 0.22 for 6% Fe concentration, 0.98 for 27%. As the iron concentration  $x$  increases, the electronic transitions of  $\text{Fe}^{2+}$  should show greater influence on the far-infrared spectra of ferropericlas. In our measurement the spectra below  $200 \text{ cm}^{-1}$  are complicated due to the presence of fringes, consequently we cannot confirm this tendency. Henning *et al.*<sup>24</sup> measured the infrared reflectance of  $\text{Fe}_x\text{Mg}_{1-x}\text{O}$  from  $x=0.4$  to 1.0 at room temperature. The  $\epsilon_2$  curves reported in their paper do not show a monotonic rise in the far-infrared region as the iron concentration  $x$  increases from 0.4 to 1.0, while  $\epsilon_2$  is always in the range of 6–10 near  $100 \text{ cm}^{-1}$ . It is difficult to explain such large  $\epsilon_2$  with lattice vibrations alone, and the accuracy of these data has been questioned.<sup>25</sup> Further experiments are needed to clarify this issue.

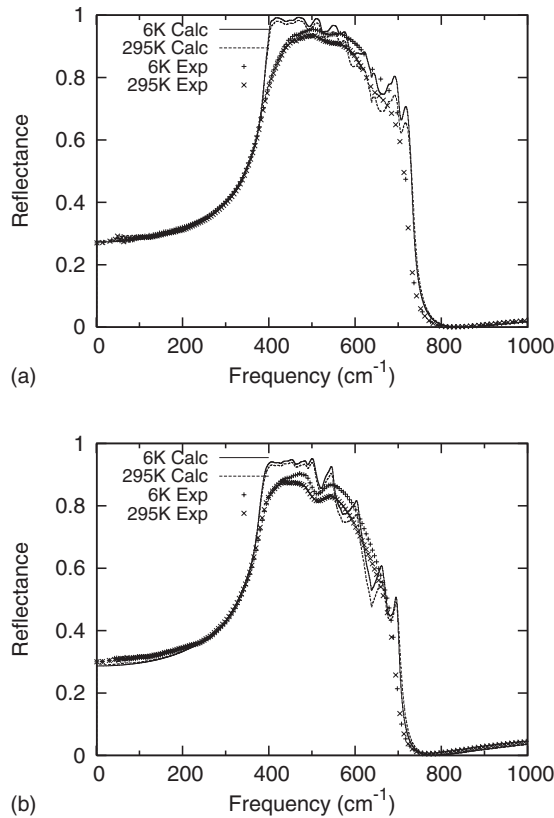


FIG. 6. The calculated infrared reflectance, compared with the experimental data [same as in Figs. 1(c) and 1(d)] for  $\text{Mg}_{1-x}\text{Fe}_x\text{O}$ . (a) 6% Fe doping; (b) 27% Fe doping.

## V. CONCLUSIONS

The infrared reflectance spectra of magnesium oxide and ferropericlase have been measured at 295 and 6 K. It is found that as iron concentration increases, the  $\epsilon_\infty$  increases, the reststrahlen frequency  $\omega_{\text{TO}}$  decreases, and the width of the TO modes remains the same in the doped materials. We construct a theoretical model which includes both disorder scattering and anharmonic phonon-phonon interactions. The model shows fairly good agreement with the experiment in the regions where the lowest-order perturbation is relatively large. Near the resonance, theory and experiment both have smaller self-energies, which makes the reflectance quite sensitive to the details. We do not know whether the disagreements with experiment in the region are caused by neglect of higher order corrections, or by inaccuracy of the underlying model. However, the model identifies the global features reasonably well, and provides a good basis for understanding the vibrational properties of ferropericlase.

## ACKNOWLEDGMENTS

Work at Stony Brook was supported by NSF ITR Grant No. ATM0426757. Work at BNL was supported by the Office of Science, U.S. Department of Energy, under Contract No. DE-AC02-98CH10886. S.D.J. was supported by NSF Grant No. EAR-0721449.

\*tsun@grad.physics.sunysb.edu

- <sup>1</sup>T. Yagi and N. Funamori, *Philos. Trans.* **354**, 1711 (1996).
- <sup>2</sup>D. M. Roessler and W. C. Walker, *Phys. Rev.* **159**, 733 (1967).
- <sup>3</sup>A. F. Goncharov, V. V. Struzhkin, and S. D. Jacobsen, *Science* **312**, 1205 (2006).
- <sup>4</sup>H. Keppler, I. Kantor, and L. S. Dubrovinsky, *Am. Mineral.* **92**, 433 (2007).
- <sup>5</sup>J. R. Jasperse, A. Kahan, and J. N. Plendl, *Phys. Rev.* **146**, 526 (1966).
- <sup>6</sup>S. D. Jacobsen, H. J. Reichmann, H. A. Spetzler, S. J. Mackwell, J. R. Smyth, R. J. Angel, and C. A. McCammon, *J. Geophys. Res.* **107**, 2037 (2002).
- <sup>7</sup>C. C. Homes, M. Reedyk, D. A. Crandles, and T. Timusk, *Appl. Opt.* **32**, 2972 (1993).
- <sup>8</sup>R. A. Cowley, *Rep. Prog. Phys.* **31**(part 1), 123 (1968).
- <sup>9</sup>*Dynamical Properties of Solids*, edited by G. K. Horton and A. A. Maradudin (North-Holland Publishing Company, Amsterdam, 1975), Vol. 2, Chap. 5.
- <sup>10</sup>J. Fabian and P. B. Allen, *Phys. Rev. Lett.* **77**, 3839 (1996).
- <sup>11</sup>J. D. Gale, *J. Chem. Soc., Faraday Trans.* **93**, 629 (1997).
- <sup>12</sup>A. M. Stoneham and M. J. L. Sangster, *Philos. Mag. B* **52**, 717 (1985).

- <sup>13</sup>M. J. L. Sangster, *J. Phys. Chem. Solids* **34**, 355 (1973).
- <sup>14</sup>M. J. L. Sangster, G. Peckham, and D. H. Saunderson, *J. Phys. C* **3**, 1026 (1970).
- <sup>15</sup>G. Kugel, C. Carabatos, B. Hennion, B. Prevot, A. Revcolevschi, and D. Tocchetti, *Phys. Rev. B* **16**, 378 (1977).
- <sup>16</sup>M. J. L. Sangster and A. M. Stoneham, *Philos. Mag. B* **43**, 597 (1981).
- <sup>17</sup>A. A. Maradudin and A. E. Fein, *Phys. Rev.* **128**, 2589 (1962).
- <sup>18</sup>E. R. Cowley, *J. Phys. C* **5**, 1345 (1972).
- <sup>19</sup>L. Bohlin and T. Högborg, *J. Phys. Chem. Solids* **29**, 1805 (1968).
- <sup>20</sup>R. J. Elliott, J. A. Krumhansl, and P. L. Leath, *Rev. Mod. Phys.* **46**, 465 (1974).
- <sup>21</sup>A. D. Bruce, *J. Phys. C* **6**, 174 (1973).
- <sup>22</sup>D. De Sousa Meneses, J. Brun, P. Echegut, and P. Simon, *Appl. Spectrosc.* **58**, 969 (2004).
- <sup>23</sup>J. Y. Wong, *Phys. Rev.* **168**, 337 (1968).
- <sup>24</sup>T. Henning, B. Begemann, H. Mutschke, and J. Dorschner, *Astron. Astrophys. Suppl. Ser.* **112**, 143 (1995).
- <sup>25</sup>A. M. Hofmeister, E. Keppel, and A. K. Speck, *Mon. Not. R. Astron. Soc.* **345**, 16 (2003).