

Ab initio calculation of electric-field–gradient tensors of forsterite

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ABSTRACT

Ab initio band-structure calculations based on the density functional theory have been performed for forsterite to obtain, with a parameter-free model, electric-field gradients for all nuclei. Calculations based on the generalized gradient approximation yield the ratio of the largest components of the calculated electric-field gradients within 1% of the experimental value for ²⁵Mg and within 2% of the experimental value for ¹⁷O. The absolute values differ by about 5%, depending on which nuclear quadrupole moment is used in the conversion. The asymmetry parameters are also in good agreement with experimental data. Values obtained with a gradient-corrected exchange–correlation potential are better than those based on the standard local-density approximation. The calculated angles between the principal axes of the quadrupole coupling tensor and the crystallographic axes agree very well with the experimental data. For the M1 site the maximum deviation is 1.8°, and for the M2 site the maximum deviation is 0.6°. The current calculations allow an evaluation of three sets of experimental data for the ¹⁷O electric-field gradient. They also confirm a proposed assignment of the measured electric-field gradient tensors to specific O atoms.

INTRODUCTION

In computational mineralogy, predictive microscopic models are increasingly used to interpret experimental data for which conflicting phenomenological explanations exist. Although reliable quantum mechanical model calculations require large computational resources, they offer the possibility of calculating rather subtle physical properties, including those due to electronic effects. Therefore, they can be applied to a large variety of problems and yield better results than conventional static lattice-energy–minimization calculations. Here we use parameter-free energy-band-structure calculations to compute electric-field gradient (EFG) tensors, which are experimentally determined by nuclear magnetic resonance (NMR), nuclear quadrupole resonance, or Mössbauer spectroscopy.

NMR has proven to be an invaluable tool for the investigation of local structural details, and, because of progress in the experimental technique, many nuclei relevant for the earth sciences can now be used. An instructive review of applications of NMR spectroscopy in the earth sciences was given by Kirkpatrick (1988). Structural information can be obtained from NMR measurements in which the interaction between the electric quadrupole moment, eQ , and the local electric-field gradient, $eq = V_{zz}$, is determined in terms of the quadrupole-coupling constant, QCC , given by $QCC = eV_{zz}Q/h$. The EFG depends on the nonspherical charge distribution around the nuclei, and its deviation from axial symmetry is defined by the asymmetry parameter, η , given by $\eta = (V_{xx} - V_{yy})/$

V_{zz} , which varies between 0 (axial symmetry) and 1. Here we follow the same conventions as in the work of Schwarz et al. (1990).

However, QCC and η cannot be derived from NMR spectra directly but must be determined by spectral simulation, which can be problematic for broad, overlapping, or weak features. Conventionally, EFGs have been explained by point-charge models, which contain adjustable parameters, such as formal charges or the Sternheimer antishielding factors. The predictive power of such parameterized calculations is limited, and the results are often ambiguous. Hence, attempts have been made to develop parameter-free calculations. For example, Tossell and coworkers [e.g., Tossell (1992) and references cited therein] used Hartree-Fock calculations on clusters to obtain NMR parameters. These calculations required the use of several approximations owing to limitations in available computing power. With a different method, which could cope with periodic lattices, Blaha et al. (1985) showed that full-potential, linearized, augmented plane-wave (FP-LAPW) calculations can be successfully used to obtain EFGs. The crucial quantity that determines an EFG is the nonspherical charge distribution close to the nucleus, which itself is directly related to chemical bonding and different occupations of the valence electrons. During the last decade, this method was used to investigate several hcp metals (Blaha et al. 1988) and many other substances, and its feasibility for complex structures, for example, was demonstrated by successful calculations for a high- T_c cuprate superconductor (Schwarz et al. 1990). From these calculations it can be deduced,

TABLE 1. Atomic coordinates used in the calculations and the corresponding remaining forces

	Hazen (1976)	Forces (GGA)	Brown (1970)	Forces (GGA)	Fujino et al. (1981)	Forces (LDA)	Forces (GGA)
Mg2 x	0.9915	0.6	0.9896	1.0	0.99169	0.0	0.4
Mg2 y	0.2774	-0.1	0.2776	-0.4	0.27739	-0.3	-0.4
Si x	0.4262	6.1	0.4226	48.6	0.42645	-1.3	2.2
Si y	0.0940	-0.9	0.0945	-4.5	0.09403	-1.9	1.4
O1 x	0.7657	18.6	0.7667	-3.4	0.76594	17.0	17.4
O1 y	0.0913	2.2	0.0918	1.7	0.09156	-0.4	1.0
O2 x	0.2215	6.6	0.2202	11.3	0.22164	4.1	4.7
O2 y	0.4474	-21.6	0.4477	-25.9	0.44705	-5.4	-14.8
O3 x	0.2777	-7.4	0.2781	-13.5	0.27751	-4.5	-5.9
O3 y	0.1628	11.9	0.1633	14.4	0.16310	2.5	8.5
O3 z	0.0331	-15.6	0.0337	-23.9	0.03304	-6.0	-12.9

Note: Forces given in mRyd/au; 1 Ryd = 13.6 eV, 1 au = 0.529 Å.

that in general FP-LAPW calculations yield EFGs within approximately 10% and asymmetry parameters within ~0.1 of the experimental values.

Considering the widespread use of NMR spectroscopy and the recent progress in quantum mechanical calculations it is worthwhile to compute electric-field-gradient tensors for silicates, which are characterized by their broad range of bond types and bond strengths. We note that NMR spectroscopy is a local technique, and therefore it is often used to investigate short-range order or local distortions. Ab initio calculations, however, exploit the periodicity of a perfectly ordered structure, so that solid solutions and the effects of short-range order are currently approximated rather crudely. Also, the present calculations are restricted to ground-state (0 K) properties.

For fully ordered structures, theoretical studies are possible and can be used for the interpretation of measured spectra, which is sometimes difficult using experimental results only. Reliable calculations allow evaluations of proposed experiments, which can be costly when isotopic enrichment is required, because they can predict NMR parameters and specify the necessary resolution. For the interpretation of spectra of silicates, correlations between structural and NMR parameters have been established (Sherriff et al. 1991; Smith et al. 1983). These studies rely on available data, which may be scarce for unusual isotopes. In theoretical studies, however, structures can be easily deformed, and thus NMR parameters as a function of structural parameters can be calculated. Also, theory can help in evaluating sets of experimental data if the latter are not in good agreement.

Forsterite, Mg_2SiO_4 , is a model system in which the same isotopes occupy different structural environments and in which the EFGs for both ^{25}Mg and ^{17}O have been studied in detail. The small differences in the Mg and O environments serve as a sensitive test for the accuracy of the calculations.

COMPUTATIONAL APPROACH

The calculations presented here are based on the density functional theory (DFT), using the local-density ap-

proximation (LDA) or the generalized gradient approximation (GGA). A recent in-depth summary can be found in the book by Singh (1994). For such calculations, one of the most accurate schemes is the LAPW method, in which the unit cell is divided into spheres centered at the atomic positions and an interstitial region. In the latter the basis set consists of plane waves that are augmented by atomic-like solutions (numerical radial functions multiplied with spherical harmonics) inside the spheres. The potential within the sphere is not restricted to have spherical symmetry, as in the older "muffin-tin" calculations but is allowed to be general, i.e., a full potential without any shape approximation is used. It is well known that DFT calculations in general give structural parameters within 1–2% of the experimental data.

In the present study, the full-potential, linearized, augmented plane-wave package, WIEN95 (Blaha et al. 1995) was used. [WIEN95 is an improved and updated version of the original copyrighted code by Blaha et al. (1990).] WIEN95 is maintained at the Technical University of Vienna and includes the capability to employ local orbitals (Singh 1991) and to calculate residual forces on atoms (Yu et al. 1991; Kohler et al. 1996). The calculation of the EFGs is based on the work of Blaha et al. (1985); a more detailed description can be found in Schwarz et al. (1990). The precision and accuracy of the calculations are controlled by only a few parameters. For the expansion of the charge density (potential) in the interstitial region a Fourier series with $|G| \leq 12$ was used. For the wave functions inside the atomic spheres angular momentum components up to $l = 12$ were included, and up to 18 k points in the irreducible wedge of the Brillouin zone were used. This corresponds to nearly 150 sampling points in the whole Brillouin zone. The cut-off for the plane-wave basis set was chosen as $k_{\max} = 4.5 a_0^{-1}$ and was checked by additional calculations, which proved that the results presented here are well converged.

RESULTS

Structure

The all-electron ab initio techniques currently in use do not yet allow a constant-pressure relaxation of low-symmetry structures. In fact, even at constant volume a relaxation of an orthorhombic structure containing 28 atoms using an all-electron approach would at present consume a prohibitive amount of computer time. Hence, in the present study all structural parameters were fixed at their experimental values. To investigate the influence of small structural distortions on the calculated physical properties we used three sets of internal structural parameters in our calculations. The atomic coordinates (Table 1) were taken from Hazen (1976), Brown (1970), and Fujino et al. (1981), but only one set of lattice parameters was used, namely the very-high-precision data given by Schwab and Küstner (1977) with $a = 4.7540$, $b = 10.1971$, and $c = 5.9806$ Å. The WIEN95 code allows the calculation of residual forces acting on the atoms using the

TABLE 2. Calculated and observed values of $V_{zz}/10^{21}$ (V/m²) for forsterite

Structure		<i>k</i> points	M1	M2	M1/M2	Si	O1	O2	O3	O1/O2	O1/O3
Hazen (1976)	LDA	6	0.99	0.91	1.09	-1.98	4.00	3.70	3.51	1.08	1.14
Hazen (1976)	GGA	6	1.08	0.92	1.17	-1.95	4.36	3.92	3.70	1.11	1.18
Hazen (1976)	GGA	18	1.08	0.92	1.17	-1.95	4.34	3.92	3.70	1.11	1.17
Brown (1970)	LDA	6	1.06	0.96	1.10	-1.39	4.47	3.52	3.24	1.27	1.38
Brown (1970)	GGA	6	1.16	0.98	1.18	1.35	4.67	3.71	3.45	1.26	1.35
Fujino et al. (1981)	LDA	6	0.98	0.90	1.09	-2.08	4.12	3.77	3.49	1.09	1.18
Fujino et al. (1981)	GGA	6	1.08	0.92	1.17	-2.02	4.31	3.96	3.70	1.09	1.16
	Exp*		1.03	0.89	1.16						
	Exp**						4.37	3.79	3.79	1.15	1.15
	Exp†						5.41	5.00	4.49	1.08	1.20
	Exp‡						4.48	4.09	3.91	1.09	1.14

Note: Conversion factors $Q(\text{mg}) = 0.20b$; $Q(\text{O}) = -0.02558b$.

* Experimental data from Derighetti et al. (1978).

** Experimental data from Schramm and Oldfield (1984).

† Experimental data from Mueller et al. (1992). The conversion from the stated quadrupole product is based on the asymmetry parameters given in Table 3.

‡ Experimental data from Fritsch et al. (1986).

formalism of Yu et al. (1991). Small residual forces provide an a posteriori justification for using high-quality structural data in the calculations without any further relaxation of the internal structural degrees of freedom.

The results are presented in Table 1, which shows that the calculated forces are small. In iterative pseudopotential calculations, where a constant-volume relaxation is comparatively simple, a structure is generally considered to be relaxed if forces are less than ~ 15 mRyd/au (~ 0.1 eV/Å). Therefore, the atomic parameters from Hazen (1976) and Fujino et al. (1981) correspond to very nearly relaxed structures, whereas this is not quite the case for the structure of Brown (1970). The present total-energy calculations confirm that the values for the *x* coordinate of the Si atom of Hazen (1976) and Fujino et al. (1981) are preferred over the value given by Brown (1970). This difference in the internal parameters has a large effect on the electric-field gradient, which is discussed below. A comparison of the forces and atomic parameters indicates, however, that generally only changes in the fourth decimal of the fractional coordinates would be necessary to relax all structures fully.

The small differences in the calculated residual forces between LDA and GGA demonstrate that for the internal degrees of freedom both approximations yield very similar structures. This is consistent with the findings by other authors (Ozolins and Körling 1993) that GGA improves on the "overbinding" of LDA and thus leads to a better agreement of cell parameters, but does not significantly change the fractional coordinates.

Electric-field gradients

The motivation for calculating EFGs of forsterite, Mg_2SiO_4 (space group *Pbnm*, $Z = 4$), was mentioned in the Introduction. Experimental data are available for ^{25}Mg and ^{17}O . The calculation of EFG tensors is challenging because both the Mg and the O atoms occupy more than one site, so relative comparisons can be made that avoid the knowledge of the (rather ill-determined) nuclear-quadrupole moment. The M1 site has site symmetry $\bar{1}$,

whereas the M2 site has site symmetry *m*. The O atoms O1 and O2 occupy sites with site symmetry *m* and a multiplicity of 4, whereas O3 occupies the general position with a multiplicity of 8. The ^{25}Mg data are those reported by Derighetti et al. (1978). For the ^{17}O NMR data, experimental values were reported by Schramm and Oldfield (1984), Fritsch et al. (1986), and Mueller et al. (1992). Mueller et al. (1992) gave for the O atoms only the products $(e^2Qq/h)(1 + \eta^2/3)^{1/2}$. To compare these with our calculated values, the asymmetry parameters must be known. Here, we used our calculated values, which agree well with the experimental data of Fritsch et al. (1986). It should be noted, though, that the data obtained by Mueller et al. (1992) are different from those of Schramm and Oldfield (1984) and Fritsch et al. (1986). The data of Schramm and Oldfield (1984) and Fritsch et al. (1986) are unambiguous with respect to the assignment of the measured values for the O3 atom only, whereas the assignment to O1 and O2 could theoretically be reversed. Mueller et al. (1992) did not attempt an assignment.

The calculated results for the EFGs are given in Tables 2–4, where they are compared to experimental data. The

TABLE 3. Calculated and observed values for the asymmetry parameter η for forsterite

Structure		<i>k</i> points	M1	M2	Si	O1	O2	O3
Hazen (1976)	LDA	6	0.92	0.44	0.74	0.32	0.43	0.19
Hazen (1976)	GGA	6	0.93	0.40	0.73	0.30	0.44	0.22
Hazen (1976)	GGA	18	0.93	0.40	0.73	0.30	0.44	0.22
Brown (1970)	LDA	6	0.65	0.38	0.70	0.30	0.52	0.25
Brown (1970)	GGA	6	0.70	0.35	0.68	0.29	0.49	0.22
Fujino et al. (1981)	LDA	6	0.91	0.42	0.73	0.31	0.45	0.23
Fujino et al. (1981)	GGA	6	0.93	0.39	0.73	0.30	0.43	0.21
	Exp*		—	0.96	0.40	—	—	—
	Exp**		—	—	—	0.3	1.0	0.2
	Exp†		—	—	—	0.28	0.39	0.18

* Experimental data from Derighetti et al. (1978).

** Experimental data from Schramm and Oldfield (1984).

† Experimental data from Fritsch et al. (1986).

TABLE 4. Observed and calculated angles between the principal axes of the quadrupole-coupling tensor and the crystallographic axes at the M1 and M2 sites

	M1			M2		
	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>
X exp	53.1	125.0	124.0	71.4	18.6	89.4
X calc	51.4	124.2	122.9	71.8	18.2	90.0
Y exp	137.8	97.8	131.1	90.0	90.6	0.6
Y calc	136.0	98.2	132.8	90.0	90.0	0.0
Z exp	72.4	36.1	120.4	18.6	108.6	90.2
Z calc	72.3	35.4	119.6	18.2	108.2	90.0

Note: Experimental data from Derighetti et al. (1978).

comparison relies on a reliable value for the quadrupole moment, Q , which is a constant for each isotope. A major problem arises from the fact that many quadrupole moments are not well known and variations of more than 10% are not uncommon. The ratio of V_{zz} values for one isotope in different sites, however, is independent of the actual value of Q and hence is a good measure of the reliability of the calculations. The calculated EFGs obtained for the structure of Brown (1970) cannot be compared to experimental values because of the poor Si position. The present calculations with GGA yield $V_{zz}(\text{M1})/V_{zz}(\text{M2}) \approx 1.17$, close to the experimental value of 1.16. The agreement is also excellent for the ratios $V_{zz}(\text{O1})/V_{zz}(\text{O2})$ and $V_{zz}(\text{O1})/V_{zz}(\text{O3})$ if the GGA calculations based on the structure of either Hazen (1976) or Fujino et al. (1981) are compared to the single-crystal data of Fritsch et al. (1986). The absolute values for the V_{zz} depend strongly on the value chosen for the quadrupole moment. For O, for which Q is well known, the agreement is satisfactory (better than 5%) for GGA calculations using the data of Schramm and Oldfield (1984) or Fritsch et al. (1986). The agreement with the data of Mueller et al. (1992) is very unsatisfactory. For Mg, small deviations occur with $Q(\text{Mg}) = 0.20b$, but deviations are larger (about 10%) if $Q(\text{Mg}) = 0.22b$. The ratio of the EFGs differs more for the experimental data for LDA than for GGA calculations, and hence the GGA is preferable in EFG studies. The LDA results, however, are still significantly better than empirical models. Derighetti et al. (1978) used a point-charge model and obtained a ratio of $V_{zz}(\text{M1})/V_{zz}(\text{M2}) \approx 1.5$, which is 30% larger than the experimentally determined value. The present calculations show that V_{zz} is positive for both the M1 and M2 sites, in agreement with the results of Derighetti et al. (1978). The effect of the poor Si position in the structure of Brown (1970) is evident from the calculated EFGs because the sign of the Si EFG is opposite to that of the other results, and on the basis of the accuracy of the current calculations the ratios of the O EFGs differ significantly from the experimental data.

The calculated asymmetry parameters, η , are given in Table 3. The effect of the choice of the exchange potential on η is small. The calculated values are in good agreement with the experimental data of Fritsch et al. (1986), and,

with one noticeable exception, with those of Schramm and Oldfield (1984). The one exception is the asymmetry parameter of the O2 atom, for which all calculations give results that are one-half the values reported by Schramm and Oldfield (1984). Hence, we conclude that the data by Fritsch et al. (1986) are preferable to those of Schramm and Oldfield (1984).

From their single-crystal work, Derighetti et al. (1978) derived the angles between the principal axes X, Y, Z of the quadrupole-coupling tensor and the crystallographic axes at the M1 and M2 sites. The calculated orientation of the electric-field-gradient tensor with respect to the crystallographic coordinates is in very good agreement, with a maximum deviation of $<2^\circ$. For the M2 site the deviation is about as large as the experimental uncertainty. The observed values are listed in Table 4 together with the calculated values from GGA calculations for the structure of Fujino et al. (1981).

DISCUSSION

The present investigation has shown that calculations such as those presented here do not necessarily rely on constant-pressure relaxations. Instead, physical properties can be calculated with good accuracy if high-quality structural data are available. The latter can be checked by inspection of the residual forces acting on the atoms. This allows the prediction of a large variety of physical properties, even in the absence of efficient relaxation algorithms. We expect that for some time this will be the most common application for all-electron calculations of complex structures.

The above calculations have also demonstrated that modern ab initio calculations are precise and sufficiently accurate to allow the calculation of EFGs and asymmetry parameters. They are in such good agreement with experimental data that they can serve as a reliable tool for checking and predicting EFGs. A significant difference between calculated and observed data constitutes a strong justification to reexamine the experimental data and their analysis. This is shown by a comparison of the three sets of data for the ^{17}O EFGs; the present calculations are in very good agreement with the data by Schramm and Oldfield (1984) and Fritsch et al. (1986), but they disagree with the data of Mueller et al. (1992). The calculations presented here also confirm that the magnitude of η for O2 obtained by Fritsch et al. (1986) is preferable to the value given by Schramm and Oldfield (1984). Furthermore, the current calculations unambiguously confirm the assignment proposed by Fritsch et al. (1986) of the EFGs to O1 and O2.

From the above calculations of forsterite we conclude that for the prediction of the EFG tensors GGA calculations provide better results than standard LDA. This is consistent with numerous other examples [Perdew et al. (1992) and references cited therein] demonstrating the improvement of density functional calculations using GGA. The same formalism can also be used to obtain NQR and Mössbauer parameters.

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