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On the elastic constants of the zeolite chlorosodalite

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The use of force-field based molecular modeling to predict the elastic constants of the zeolite chlorosodalite is described. Theoretical predictions of the on-axis and off-axis elastic constants strongly suggest that an error exists in the published elastic constants of the material. When the previous experimental data are corrected by transposing the published directional ultrasound velocities, excellent agreement is observed between the off-axis plots of sodalite produced by experiment and modeling. Further confirmation of the prediction is supplied by considering the Zener ratios of other inorganic materials that possess cubic symmetry. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2162859]

Zeolites are nanoporous silicates, both naturally occurring minerals and synthetic materials, with widespread applications in catalysis, separation science, and ion exchange.[1] Their atomic-scale structures, constructed from corner-shared tetrahedral silicate and aluminate units which encapsulate exchangeable cations and water molecules, have been the focus of study for a good many years because of these considerable practical uses. Recently several groups have begun to investigate the elastic properties of zeolite structures using various computational methods.[2–4] One of these studies has predicted rather unusual properties: for example, by considering siliceous forms of zeolites (i.e., polymorphs of SiO_2), it has been proposed that many zeolite frameworks should possess negative Poisson's ratios, implying a counterintuitive lateral widening upon application of longitudinal stress in certain directions.[2]

In order to verify the predicted elastic properties of zeolites, it is important to have access to experimental data concerning elasticity. Such data would also provide an important means of validation of the force fields used in performing simulations of the solid state. Of the numerous zeolites now known, however, the only three zeolites for which single-crystal elastic constants have been measured are chlorosodalite, $Na_8(Al_6Si_6O_{24})Cl_2$,[5] natrolite, $Na_2(Al_2Si_3O_{10}) \cdot 2H_2O$,[6,7] and analcime, $Na_{16}(Al_{16}Si_{32}O_{96}) \cdot 16H_2O$.[7] Elastic constants have also been reported for a related material, dodecasil-3C, a silica clathrate which contained guest molecules,[8] but in general there is a dearth of elastic data for these open-framework silicate structures. Here we report molecular simulation data which strongly suggest that in one of these previous reports an error exists in the ultrasound data reported for naturally occurring single crystals of chlorosodalite.

We have used the molecular modeling package Cerius[2] v. 4.8.1 (Accelrys, San Diego, CA), which allows the implementation of a variety of force fields, to simulate the atomic structure of chlorosodalite (cubic, $P\bar{4}3n$, $a = 8.882$ Å).[9] This package has been widely used to simulate zeolite structures and their interaction with guest molecules.[10–13] The energy

expressions E were set up using parameters from the consistent valence force field (CVFF) force field[14] and nonbond terms were added using the Ewald summation technique. The minimum energy configurations were derived by minimizing the potential energy as a function of the atomic coordinates and unit cell parameters to the default Cerius[2] high convergence criterion. No constraints on the shape or size of the unit cell were applied during minimisation. The 6×6 stiffness matrix **C** (and its inverse, the compliance matrix **S**) of the minimum energy single crystalline chlorosodalite system was calculated from the second derivative of the potential energy function since

$$c_{ij} = \frac{1}{V}\frac{\partial^2 E}{\partial \varepsilon_i \partial \varepsilon_j} \quad i,j = 1,2,\ldots,6, \tag{1}$$

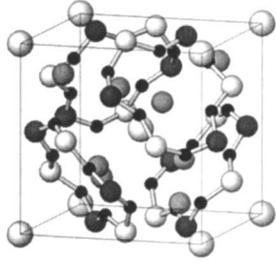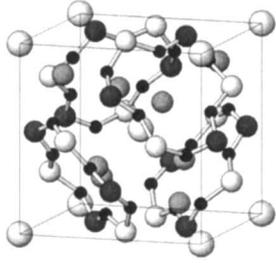where c_{ij} is a component of the stiffness matrix, **C**, E is the energy expression, V is the volume of the unit cell, and ε_i and ε_j are strain components.

Table I shows the structure, cell parameter, and unique atomic coordinates of the experimental chlorosodalite structure of McMullan *et al.*,[9] determined using powder neutron diffraction, in comparison with that of the simulated structure. Interatomic distances generated using the crystal data from experiment and modeling agree within ±0.02 Å, demonstrating that we are able to reproduce accurately the atomic-scale structure of chlorosodalite. Table II compares the predicted on-axis elastic constants for the material with those reported by Li *et al.*,[5] and also values produced by inverting the reported [100] and [110] ultrasound velocities. The data in Table II alone do not highlight any discrepancy between modeling and reported elastic constants: the magnitude of the predicted elastic constants could be consistent with either interpretation of the experimental data. If however, off-axis polar plots of Poisson's ratio and Young's moduli are calculated using the formulas presented by Hearmon,[15,16] Fig. 1, then there is a clear difference between the simulated values and the reported constants. Upon rotation about x, the modeling data show a minimum value for the Young's modulus E_y/E_z at 45° while plots generated using the published elastic constants show a maximum value of

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TABLE I. The experimental and simulated unit cell of chlorosodalite. Silicon atoms: large dark grey spheres, aluminium: large white spheres; oxygen: small black spheres, sodium: large pale grey spheres and chlorine: large white spheres. Bonds are shown between aluminium and oxygen, and silicon and oxygen.

	Experimental[9]	Simulated
Structure		
$a = b = c$ (Å)	8.882	8.848
Na1 x,y,z	0.17780, 0.17780, 0.17780	0.17937, 0.17937, 0.17937
Si1 x,y,z	0.25, 0, 0.5	0.25, 0, 0.5
Al1 x,y,z	0.25, 0.5, 0	0.25, 0.5, 0
O1 x,y,z	0.13925, 0.43851, 0.14954	0.13416, 0.43525, 0.14782
Cl1 x,y,z	0, 0, 0	0, 0, 0

E_y/E_z at this rotation. A similar trend is observed for the Poisson's ratios: ν_{yx} is at a minimum and ν_{yz} is at a maximum at 45° to the axis for the modeled data while for the published elastic constants, ν_{yx} is at a maximum and ν_{yz} is at a minimum at this rotation. In order to correct this disagreement, the reported sound velocities which were measured for the [100] and [110] crystal directions simply need to be swapped. The form of the off-axis plots, Fig. 1, then shows excellent agreement with the experimental data. This suggests an error in either manipulation of the single crystal specimen, or in reporting the experimental data, in the original publication.

A convenient way of quantifying the degree of off-axis anisotropy in the elastic constants for a cubic crystal is to use the Zener ratio $[Z=2 \cdot C_{44}/(C_{11}-C_{12})]$.[17] The elastic constants of a number of materials with cubic crystal symmetry have been reported[18] and it may be observed that the Zener ratio takes a wide range of values, from 0.4 for KCl[19] to 2.4 for MgAl$_2$O$_4$,[20] for example. Those materials with closely related atomic compositions and structures, however, exhibit similar Zener ratios: for example, the rock-salt oxides MnO and CoO have Zener ratios of 1.41 and 1.43, respectively,[21] while for the ternary, spinel-type oxides Fe$_3$O$_4$ and FeCr$_2$O$_4$ the values of 1.12 and 1.32, respectively, are found.[21] This is

not surprising as the elastic constants depend on the crystal structure and interatomic forces. Analcime is the only other cubic aluminium silicate zeolite for which elastic constants have been measured, and this has a Zener ratio of 0.71,[7] close to the predicted Zener ratio of 0.74 for chlorosodalite. By comparison, the Zener ratio calculated from the original experimental data for chlorosodalite is 1.46 whereas the Zener ratio using the corrected experimental data is 0.72. Figure 2 shows off-axis plots of Youngs's moduli and Poisson's ratios of analcime, spinel, MgAl$_2$O$_4$, and potassium chloride, KCl. This demonstrates the sensitivity of these plots to the chemical nature, and hence, atomic structure, of the material studied, and therefore how these data must also be used as a test of any simulated elastic data, in addition to the on-axis values of elastic constants. The similarity of the polar plot for analcime and the corrected plot for chlorosodalite, further backs our conclusion that the published elastic constants for chlorosodalite are incorrect due to transposition of experimental data.

TABLE II. The on-axis mechanical properties of chlorosodalite from the reported ultrasound data, corrected ultrasound data, and modeling predictions.

	Ultrasound data[a]	Corrected ultrasound data	Modeling predictions
C_{11}/GPa	88.52	100.05	144.9
C_{12}/GPa	38.70	24.90	38.58
C_{44}/GPa	36.46	27.16	39.27
E/GPa	64.98	88.45	128.7
ν_{xy}	0.304	0.213	0.210
G/GPa	36.46	24.89	39.27
K/GPa	55.30	51.45	74.03

[a]See Ref. 5.

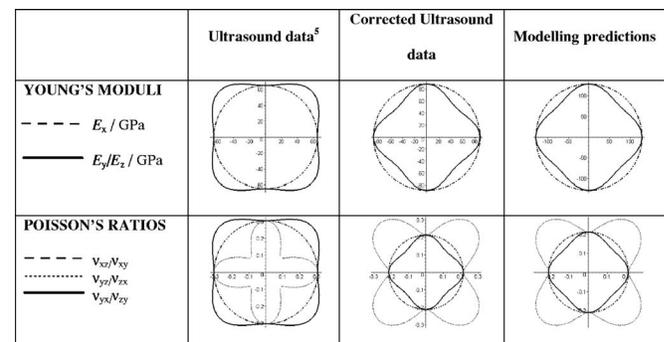|	Ultrasound data[5]	Corrected Ultrasound data	Modelling predictions
YOUNG'S MODULI			
- - - E_x / GPa			
—— E_y/E_z / GPa			
POISSON'S RATIOS			
- - - ν_{xz}/ν_{xy}			
⋯⋯ ν_{yz}/ν_{zx}			
—— ν_{yx}/ν_{zy}			

FIG. 1. Off-axis plots produced by rotation about the x axis for the previously reported Young's moduli and Poisson's ratios, the corrected elastic constants and those predicted using molecular modeling using the CVFF_300 force field of chlorosodalite.
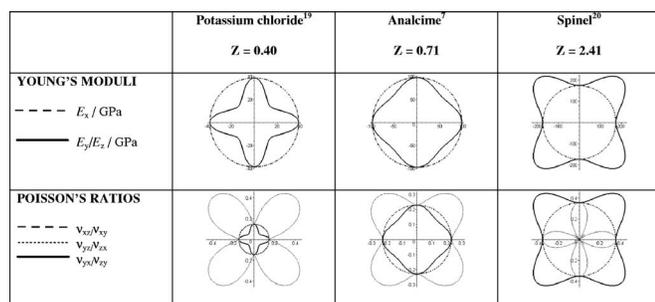
	Potassium chloride[19] Z = 0.40	Analcime[7] Z = 0.71	Spinel[20] Z = 2.41
YOUNG'S MODULI			
- - - - E_x / GPa			
—— E_y/E_z / GPa			
POISSON'S RATIOS			
- - - - ν_{xz}/ν_{xy} · · · · ν_{yz}/ν_{zx} —— ν_{yx}/ν_{zy}			

FIG. 2. Off-axis plots produced by rotation about the x axis for the Young's moduli and Poisson's ratios of the cubic materials potassium chloride, KCl, analcime, $Na_{16}(Al_{16}Si_{32}O_{96}) \cdot 16H_2O$, and spinel, $MgAl_2O_4$. The value of Zener ratio, Z, is quoted for each material.

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