Si-doping effect on bonding nature and elasticity of Al*M*B_{14} with *M*=Li, Mg, and Na

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Si-doping effect on bonding nature and elasticity of AlMB$_{14}$ with M=Li, Mg, and Na

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Abstract. We study the effects of Si doping on the bonding nature and elastic properties of AlMB$_{14}$ compounds having B$_{12}$ icosahedral clusters with M = Li, Mg, and Na, by means of *ab initio* calculations. We find that Si substitution leads to a decrease in the cohesive energy as well as in the values of the bulk, shear, and Young's moduli.

1. Introduction

Boron-rich compounds containing B$_{12}$ icosahedral clusters are of great technological interest because of their high hardness. A variety of compounds have been made by doping metal/carbon species in the void space between the boron icosahedra. Among these, the AlMB$_{14}$-type compounds are simple, and many experimental studies have been carried out in recent years [1, 2, 3] after the discovery [4] of AlMgB$_{14}$. However, theoretical studies of these compounds are few[5, 6]. One reason for the slow progress has been the large number of atoms (64) in the unit cell of this compound as shown in figure 1. This makes *ab initio* calculations of such materials computationally very demanding. Also there are no experimental reports of elastic properties because it is difficult to make single crystals of these compounds. With the development of faster computers, calculations of such large pure and doped systems can be done now routinely. Of particular interest is the doping of Si that has been reported to enhance hardness of AlMgB$_{14}$ compound [7]. However, it is not yet understood what leads to an increase in the hardness. Here we report calculations on the effects of Si doping on the structural, electronic, and the elastic properties of such boron rich compounds.

The unit cell of AlMB$_{14}$ compound (figure 1) has four formula units (64 atoms) in an orthorhombic structure with space group *Imma*. Each B$_{12}$ icosahedron is constructed of four crystallographically independent boron atom sites, namely two B1, four B3, four B4, and two B5 sites. There are eight boron sites in the unit cell denoted as B2 type[3] that lie in between the B$_{12}$ icosahedra. Each boron atom on an icosahedron is connected to another boron atom either on a neighboring icosahedron or with a bridging B2 atom. Changing the M atoms such as Li or Mg, as well as the doping of Si, affects the number of valence electrons in the unit cell and possibly the volume. It could also affect the local bonding nature particularly around the Si sites.

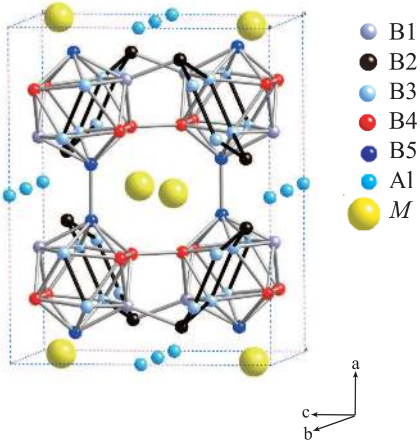


Figure 1. Unit cell of AlMB$_{14}$.

In an earlier paper, we have reported the results of *ab initio* calculations on the atomic and electronic structures as well as the elastic properties of AlMB$_{14}$, M = Li, Na, and Mg compounds. We showed that Mg compounds are metallic while Li and Na compounds are semiconducting with quite different band gaps. It was also shown that there exists an asymmetric covalent bonding between B$_{12}$ icosahedra that, together with a void along the b axis, leads to an asymmetric dependence of the elastic properties when M is varied. We also explored the changes in the properties when Al or M atoms were replaced by Si [8]. *Ab initio* studies of Si doping in AlMgB$_{14}$ by other researchers [7] have been carried out using the local density approximation, and it has been shown that addition of Si decreases the elastic properties. This contradicts to the experimental results that have shown an increase in hardness by addition of Si. In these studies by Cook *et al.* Si substitution was done on Al sites[7] and the possibility of substitution on other sites was not explored.

The aim of this paper is to understand the effects of Si doping on the bonding character in boron-rich AlMB$_{14}$ compounds with M = Li, Mg, and Na and to explore substitution of Si atoms on Al or M or B1, B2, or B3 sites. Furthermore we also varied the number of Si atoms in the unit cell up to a maximum of sixteen atoms and analyzed the cohesive energy, the density of states, and the charge density to understand the changes due to Si substitution. We also explored Si atom in an interstitial site as there is a void in the unit cell. In Sec. 2, we discuss our calculation procedure. The results are given in Sec. 3 and a summary in Sec. 4.

2. Calculation

We follow the procedure of ref. [8] and use the projector augmented wave method [9, 10] as implemented in the Vienna *ab initio* simulation package [12, 11]. The exchange-correlation energy is calculated within the generalized gradient approximation [13]. The free energy is minimized over the degrees of freedom of both the electron density and the ionic positions using conjugate-gradient iterative minimization technique. The cut-off energy for the plane wave expansion is taken as 477.97 eV. The Brillouin zone integrations are performed using a set of $8 \times 8 \times 8$ **k**-points in all cases. Direct optimization of the cell gave the lattice constants, a, b, and c. The Murnaghan equation of state [14] is used to determine the bulk modulus, B_M, for a single crystal by fitting the total energy at various volumes of the cell. For orthorhombic crystals, we calculated nine elastic constants, C_{11}, C_{22}, C_{33}, C_{44}, C_{55}, C_{66}, C_{12}, C_{13}, and C_{23}, and the derivative of the energy as a function of the lattice strain [15] δ which is taken as 0.005 and 0.01 in all cases.

For a statistically isotropic polycrystalline single phase material, the bulk modulus B and the shear modulus, G are related to the elastic constants following the Voigt approximation [16] or the Reuss approximation [17]. The Voigt approximation assumes a uniform strain and gives the bulk modulus, B_v, and the shear modulus, G_v, as $B_v = 1/9(C_{11}+C_{22}+C_{33})+2/9(C_{12}+C_{23}+C_{13})$ and $G_v = 1/15(C_{11} + C_{22} + C_{33}) - 1/15(C_{12} + C_{13} + C_{23}) + 1/5(C_{44} + C_{55} + C_{66})$. The Reuss approximation assumes a uniform stress and gives the bulk modulus, B_R, and the shear modulus, G_R, as $B_R = 1/((s_{11} + s_{22} + s_{33}) + 2(s_{12} + s_{13} + s_{23}))$ and $G_R = 15/(4(s_{11} + s_{22} + s_{33}) - 4(s_{12} + s_{13} + s_{23}) + 3(s_{44} + s_{55} + s_{66}))$. Here s_{ij} are the compliance constants. These equations give the theoretical maximum (Voigt approximation) and minimum (Reuss approximation) values of the average isotropic elastic moduli of a polycrystalline sample using the anisotropic single crystal elastic constants. Finally we arithmetically averaged the values obtained from Voigt approximation and Reuss approximation following Hill *et al.* [18] to estimate the elastic properties of a polycrystalline sample. Accordingly the bulk modulus and shear modulus of a polycrystalline sample are obtained from $B = (B_v + B_R)/2$ and $G = (G_v + G_R)/2$, respectively. The Young's modulus, Y, and the Poisson ratio, ν, are estimated from $Y = 9BG/(3B + G)$ and $\nu = (3B - 2G)/2(3B + G)$.

In order to understand the effects of Si doping, we considered model systems in which Si is substituted on Al, M, B_1, B_2, or B_3 sites. We explored substitution on Al sites in detail taking $\mathrm{Al}_{4-x}\mathrm{Si}_x\mathrm{M}_4\mathrm{B}_{56}$ compounds with x = 1-4. For x = 1 and 2 we further studied different possible Al sites in order to find the minimum energy configuration. For Al and Li sites, the maximum number of Si atoms considered is four, whereas for Si on boron sites (B_1, B_2, or B_3), the maximum number of Si atoms is sixteen. Furthermore, Si doping at interstitial site (0.5 0.5 0.5) is also treated in the case M = Mg. In each case, the structure is reoptimized. For comparison, the cases without Si doping are also shown by taking results from ref. [8].

3. Results and discussion

Tables 1 - 3 show the calculated cohesive energy, optimized lattice constants, a, b, and c, and the bulk modulus, B_M for M = Li, Mg, and Na, respectively, obtained using Murnaghan equation of state for some configurations. Note that there is slight lattice distortion when adding one Si atom.

From table 1, it is clear that in all cases, Si substitution lowers the cohesive energy and with increasing x, it decreases more significantly. By comparing the cases of Si substitution on either bridging B2 or B1/B3 sites that construct boron icosahedral cluster and connect with bridging B2 sites, we find that among these boron sites, the B3 site is energetically most favorable. However, these are not the best sites for Si doping. Substitution on M = Li or Mg site costs the least energy, while for M = Na, substitution on Al site is energetically the best. Furthermore, by comparing the energies in the cases of one Si substitution on Al sites, we find that the cohesive energy is nearly the same for all Al sites. However, when two Si atoms replace two Al atoms, substitution on two neighboring Al sites in the unit cell ($\mathrm{Al}_2\mathrm{Li}_4\mathrm{Si}_2\mathrm{B}_{56}$-2) is most favorable. In the case of substitution on Li sites, we considered the compound $\mathrm{Al}_4\mathrm{Li}_{4-x}\mathrm{Si}_x\mathrm{B}_{56}$ with x = 1. The cohesive energy decreases compared with the undoped case. The substitution of a Si atom on a Li site is favorable by 0.003 eV/atom as compared to substitution on an Al site. The lattice constants a, b, and c for substitution on an Li site are 10.37, 5.88, and 8.14 Å, respectively as compared to the values 10.35, 5.85, and 8.14 Å for the undoped case. Therefore, there is a slight expansion of the lattice by Si substitution on Li sites, while Si substitution on Al sites decreases the lattice volume compared with the undoped case. However, the volume change is quite small for substitution on Al or M sites, and therefore such sites are the likely candidates for

Table 1. Cohesive energy, lattice constants, and the bulk modulus, in the case of M=Li

number and site of Si substitution	configuration	cohesive energy (eV/atom)	a (Å)	b (Å)	c (Å)	B_M (GPa)
0	$Al_4Li_4B_{56}$ [8]	6.100	10.350	5.850	8.140	211
one Al-site	$Al_3Li_4Si_1B_{56}$-1	6.079	10.336	5.856	8.138	-
one Al-site	$Al_3Li_4Si_1B_{56}$-2	6.079	10.336	5.856	8.138	-
one Li-site	$Al_4Li_3Si_1B_{56}$	6.082	10.373	5.882	8.136	191
one B1-site	$Al_4Li_4Si_1B_{55}$	6.021	10.410	5.898	8.173	-
one B2-site	$Al_4Li_4Si_1B_{55}$	6.030	10.427	5.939	8.161	-
one B3-site	$Al_4Li_4Si_1B_{55}$	6.032	10.411	5.914	8.153	-
two Al-sites	$Al_2Li_4Si_2B_{56}$-1	6.060	10.314	5.862	8.138	-
two Al-sites	$Al_2Li_4Si_2B_{56}$-2	6.066	10.332	5.855	8.151	-
two Al-sites	$Al_2Li_4Si_2B_{56}$-3	6.061	10.314	5.860	8.138	-
two Al-sites	$Al_2Li_4Si_2B_{56}$-4	6.061	10.314	5.860	8.138	-
four Al-sites	$Al_0Li_4Si_4B_{56}$	6.034	10.295	5.854	8.163	191
four Li-sites	$Al_4Li_0Si_4B_{56}$	6.028	10.467	5.920	8.139	179
eight B2-sites	$Al_4Li_4Si_8B_{48}$	5.630	10.785	6.528	8.298	144

Table 2. Cohesive energy, lattice constants, and the bulk modulus, in the case of M = Mg

number and site of Si substitution	configuration	cohesive energy (eV/atom)	a (Å)	b (Å)	c (Å)	B_M (GPa)
0	$Al_4Mg_4B_{56}$ [8]	6.006	10.360	5.910	8.120	211
one Al-site	$Al_3Mg_4Si_1B_{56}$-1	5.993	10.346	5.911	8.137	197
one Al-site	$Al_3Mg_4Si_1B_{56}$-2	5.993	10.346	5.911	8.137	197
one Mg-site	$Al_4Mg_3Si_1B_{56}$	6.001	10.370	5.906	8.150	196
one B1-site	$Al_4Mg_4Si_1B_{55}$	5.930	10.430	5.935	8.179	194
one B2-site	$Al_4Mg_4Si_1B_{55}$	5.936	10.461	5.973	8.173	191
one B3-site	$Al_4Mg_4Si_1B_{55}$	5.936	10.441	5.951	8.159	194
eight B1-sites	$Al_4Mg_4Si_8B_{48}$	5.554	10.863	6.322	8.766	150
eight B2-sites	$Al_4Mg_4Si_8B_{48}$	5.554	10.862	6.322	8.764	150
eight B3-sites	$Al_4Mg_4Si_8B_{48}$	5.548	10.949	6.127	8.621	171
sixteen B3-sites	$Al_4Mg_4Si_16B_{40}$	5.232	11.034	6.254	9.602	143
one interstitial Si	$Al_4Mg_4Si_1B_{56}$	5.921	10.545	5.922	8.204	181

Si substitution. Note that the substitution on boron sites leads to a significant lattice expansion.

The bulk modulus, B_M, decreases to 191 GPa by changing one Si atom on Li site. Such a decrease was also found by Lowther for Si substitution in $AlMgB_4$. However, in this study Si was substituted on an Al site. Our calculations show that Si substitution is energetically more favorable on Mg site, though there is a small decrease in the cohesive energy as compared to the undoped case. The elastic properties also show a decrease and there is a small expansion in the unit cell volume. Furthermore we find that in general, an increase in the number of Si atoms decreases B_M more significantly. When adding one interstitial Si atom at (0.5 0.5 0.5) site of $Al_4Mg_4B_{56}$, the bulk modulus and the cohesive energy per atom again decrease compared with the case of no interstitial Si addition. For example, the B4-B4, B5-B5, and B4-B5 bond lengths increase from 1.758, 1.722, and 1.789 to 1.799, 1.829, and 1.830, respectively. An increase in the B-B bond lengths affects the bonding between boron atoms and decreases the bulk modulus.

Table 3. Cohesive energy, lattice constants, and bulk modulus, in the case of M = Na

number and site of Si substitution	configuration	cohesive energy (eV/atom)	a (Å)	b (Å)	c (Å)	B_M (GPa)
0	$Al_4Na_4B_{56}$ [8]	6.045	10.470	5.850	8.230	209
one Al-site	$Al_3Na_4Si_1B_{56}$-1	6.025	10.455	5.851	8.235	-
one Al-site	$Al_3Na_4Si_1B_{56}$-2	6.025	10.455	5.851	8.235	-
one Na-site	$Al_3Na_4Si_1B_{56}$	6.022	10.449	5.856	8.229	189
one B1-site	$Al_4Na_4Si_1B_{55}$	5.965	10.527	5.893	8.272	-
one B2-site	$Al_4Na_4Si_1B_{55}$	5.975	10.549	5.930	8.271	-
one B3-site	$Al_4Na_4Si_1B_{55}$	5.976	10.528	5.909	8.251	-
eight B2sites	$Al_4Na_4Si_8B_{48}$	5.561	10.950	6.477	8.530	144

In the row Li, Na, or Mg to Si, the $3p$ orbitals start playing an increasingly important role. Therefore, it is useful to analyze the electronic structure and the charge density distribution. Considering substitution on boron sites, we find that for all M, replacing eight bridging B2 atoms in the unit cell by Si leads to a significant decrease in the cohesive energy; the lattice constants increase and the bulk modulus B_M decreases. In order to further check particularly the case of M = Mg, we replaced eight boron atoms on B1 or B3 sites with Si. For substitution on boron sites, the highest B_M is realized when Si is substituted on B3 sites. However, the absolute value of B_M decreases compared with the undoped case. The decreasing tendency of B_M with increasing x became more significant when all the sixteen boron atoms on B3 sites are replaced by Si. In this case with M = Mg, B_M becomes 143 GPa as compared to the value of 211 GPa for the undoped case.

In order to understand the effect of Si doping on the elastic properties, we have given in table 4 the elastic constants, the bulk, shear and Young's moduli, and the Poisson ratio. The bulk modulus obtained using the Murnaghan equation of state is given in table 1. In order to obtain shear modulus, we considered a hypothetical case where all M or all Al atoms are replaced by Si in order to keep the same symmetry. That is, we calculated the elastic constants in the cases of $Al_4Si_4B_{56}$ and $Si_4Li_4B_{56}$. In general, our results show that all the elastic constants, shear, bulk, and Young's moduli decrease by replacing M or Al by Si compared to the values of $AlMB_{14}$, which can be seen in tables 1-3 of this paper and table 2 of ref. [8]. However, the values for $Si_4Li_4B_{56}$ are significantly higher than in case of $Al_4Si_4B_{56}$. Therefore, our results suggest that the effect of Si doping is more than a substitutional effect from the point of view of observed increase in hardness.

In order to understand the difference in the bonding character when Si is substituted, we have plotted in figure 2 the partial and the total densities of states (DOS) for the case of one Si atom doped on a Li site, namely for the compound $Al_4Li_3SiB_{56}$. The main contribution to the total DOS comes from $2s$ and $2p$ orbitals of boron atoms, which hybridize strongly on the nearest neighbor sites and have three center bonding on boron icosahedra as in undoped $AlLiB_{14}$ [8]. However, in contrast to $AlLiB_{14}$, for which there is little charge around the Li sites, as one can see in figure 2, there is significant density of states on Si in the occupied region for the Si doped system. The Fermi energy lies in a band and therefore, similar to the case of M = Mg, an increase in the number of electrons by substitution of Si makes the $AlLiB_{14}$ compound metallic. That is, substitution of Si could result in different transport properties of these compounds leading to new applications.

Figure 3 shows the isocontours of the total charge density and the difference in the charge densities of $Al_4Li_3SiB_{56}$ and the sum of the charge densities of a hypothetical case of $Al_4Li_3B_{56}$ (Si atom removed leaving the positions of the remaining atoms unchanged) and an isolated Si

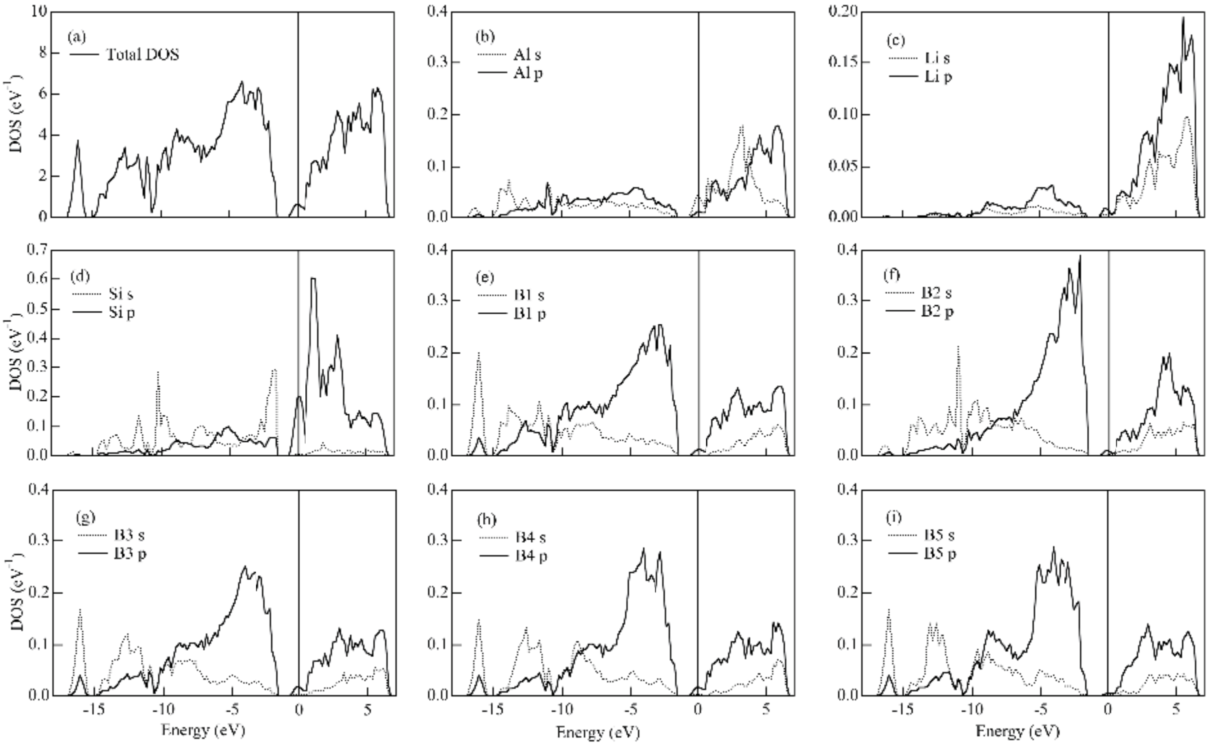
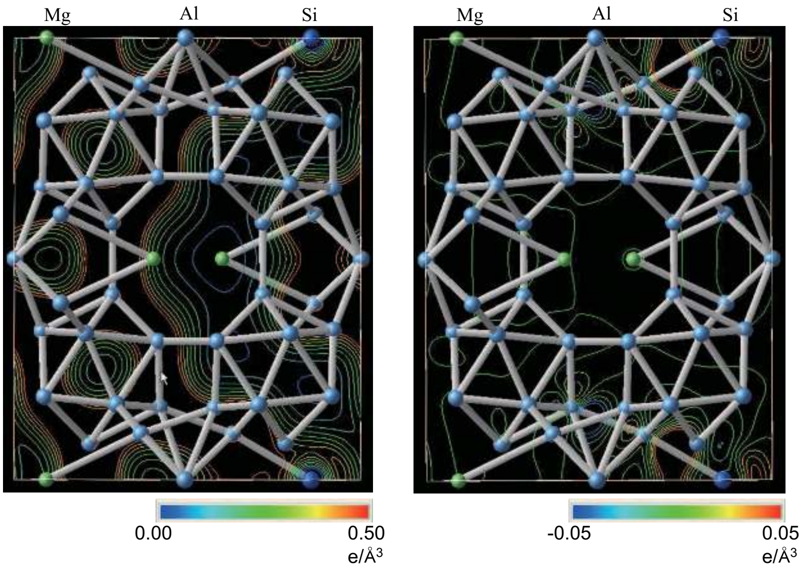


Figure 2. (a) Total DOS and (b-i) site-projected partial DOS on Al, Li, Si, B1, B2, B3, B4, and B5 atoms for the Si doped case ($Al_4Li_3SiB_{56}$), respectively. The Fermi energy is at the zero of energy.

Table 4. Elastic properties obtained by the present calculations in the unit of GPa

	$Al_4Si_4B_{56}$	$Si_4Li_4B_{56}$		$Al_4Si_4B_{56}$	$Si_4Li_4B_{56}$
C_{11}	412	447	B_v	179	193
C_{22}	474	517	B_R	177	191
C_{33}	394	439	B	178	192
C_{44}	180	197	G_v	173	181
C_{55}	164	135	G_R	171	175
C_{66}	48	162	G	172	175
C_{12}	44	27	Y	391	408
C_{13}	48	42	ν	0.13	0.15
C_{23}	72	98			

atom on the same position. The total charge density (figure 3a) has overall similar behavior as in $AlLiB_{14}$. There is a 3-D network of strongly bonded boron icosahedra and, as one could expect from the partial DOS of Si, we find electronic charge around Si ions. There is excess charge between neighboring icosahedra (figure 3b) primarily along a direction resulting from a contraction of charge (see figure 3 for the depletion of charge) between faces of two neighboring icosahedra that have B1, B3, and B5 atoms. Therefore, our results suggest that Si doping enhances inter-cluster covalent bonding in one direction.



(a) (b)

Figure 3. (a) Isocontours (values from 0 to 0.05 e/Å^3 with an increment of 0.005 e/Å^3) of the total electronic charge density for Si doped case ($Al_4Li_3SiB_{56}$), (b) isocontours (values from -0.05 to +0.05 e/Å^3 with an increment of 0.005 e/Å^3) of the difference between the charge density of $Al_4Li_3SiB_{56}$ and the such of the charge densities of a hypothetical case of $Al_4Li_3B_{56}$ and an isolated Si atom (positive and negative value show excess and depletion, respectively).

4. Summary

In summary, we have studied the effects of Si doping in $\mathrm{Al}M\mathrm{B}_{14}$ compounds having B_{12} icosahedral clusters with M = Li, Mg and Na by means of first principles calculations. By replacing Si atoms systematically on Al, M, B1, B2, or B3 sites and estimating the cohesive energy and the elastic properties, we find that Si substitution leads to a decrease in the cohesive energy as well as in the values of the bulk, shear, and Young's moduli.

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