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# Short range potential parameters and electronic polarizabilities of $\beta$ -Ga<sub>2</sub>O<sub>3</sub>

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## Abstract

In this work we formulate and build algorithms based on the modified polarizable point ion model for simulating low symmetry perfect crystals in order to study the interionic interactions of the constituent ions. A set of potential parameters and electronic polarizabilities are computed for monoclinic  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> by optimizing the crystal with respect to the structural parameters and the static dielectric constant. The calculated polarizabilities of the participating ions are found to be significantly lower in the crystal environment than the free ion values. Stability of the optimized crystal has been verified by testing the positive definiteness of the Hessian matrix.

## 1. Introduction

Atomistic simulations of low symmetry materials are usually difficult for variety of reasons. Such structures are complex and have large numbers of ions per unit cell. So, the number of independent variables becomes very large. More importantly, even in perfect crystals the electric fields at ionic sites do not vanish. If the ions are highly polarizable, the electric fields polarize the ions and even though net polarization is absent, individual ions have dipole moments. In simulations based on the shell model [1], electronic polarizations of ions are treated by means of springs connecting the cores and shells constituting the ions. Hence the shell model only deals with rigid monopole charges, though the numbers of monopoles are double those of ions. Here, the low symmetry adds to the complexity only by increasing the number of independent variables, but the formulation is exactly same and straightforward.

In contrast to the shell model, the polarizable point ion (PPI) model [2] becomes complex in formalism for low symmetry crystals. For this reason, atomistic simulations in various PPI models [3, 4] have been restricted to high symmetry structures, mostly the simple cubic structures. Usually in high symmetry materials, ions in perfect crystals do not have dipole moments. Hence the short range potentials can be obtained by optimizing the crystals with rigid ion approximation. With the low symmetry crystals, we must evolve a method for obtaining the short range potentials in the presence of ionic dipoles.

Another difficulty that arises in simulating low symmetry crystals with models based on PPI is the lack of knowledge of electronic polarizabilities. Free ion values of electronic polarizabilities overestimate the polarizations in defect calculations. The polarizabilities in the crystal environment are usually suppressed. The modified polarizable point ion (MPPI) model [3] has clearly demonstrated this point. In MPPI, since the short range potentials are already known, displacement polarizabilities are calculated using the force constants which in turn are used to calculate the electronic polarizabilities. The generalization of this procedure to low symmetry crystals is not straightforward, since the perfect crystal simulation itself must use electronic polarizabilities. Thus the electronic polarizabilities and short range parameters must be simultaneously deduced using perfect crystal optimizations.

In spite of its sound physical background, one disadvantage with the shell model is the large number of variables associated with the calculations. Due to this, it is not feasible to extend the shell model formalism beyond the dipolar approximation. On the other hand, the PPI model has been extended to the EPPI (extended PPI) model which successfully includes quadrupoles in some high symmetry crystals [4–6] and the contributions were found to be quite significant. It is expected that the quadrupolar contribution will be even more prominent in the case of low symmetry crystals. It therefore seems logical to first generalize the PPI models to low symmetry structures so that later on the effect of quadrupoles can also be tested in them.

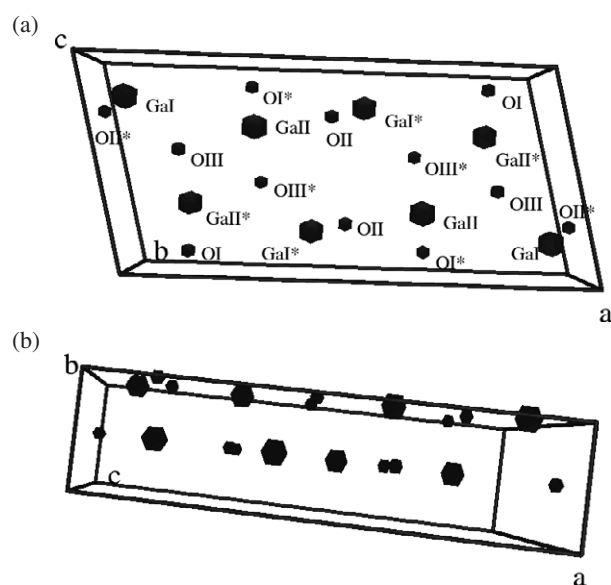
The motivation behind this work is twofold. First, the formalism of MPPI (and later, EPPI) models needs be generalized to include low symmetry materials. These models have been very successful in atomistic simulation of high symmetry materials, mostly cubic. Secondly, to make these calculations accessible to materials scientists, we need to develop packages like GULP [7] or HADES [8]. These packages were built on the shell model and are very popular. There is a lack of such packages for MPPI models. In the present work, first we formulate and build algorithms based on MPPI models for simulating low symmetry perfect crystals and then find a set of potential parameters and electronic polarizabilities for monoclinic  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> using these codes.

$\beta$ -Ga<sub>2</sub>O<sub>3</sub> is the most stable phase at room temperature out of the five existing phases ( $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  and  $\epsilon$ ) [9] of Ga<sub>2</sub>O<sub>3</sub>. It is intrinsically an insulator with a band gap of 4.8 eV. However when synthesized under reducing conditions, the material becomes an n-type semiconductor [10]. In gallium oxide, the gallium and oxygen atoms are bonded ionically. This material has wide applications in the fields of materials science and optoelectronics. It is used as a component in preparing the anodic oxide on GaAs which has drawn subsequent attention in the semiconductor industry [11] and also acts as an important maser material when doped with Cr<sup>3+</sup> [12]. Recently, it has found its application as an ultraviolet transparent conducting oxide in excimer lasers [13] and has also been used as a gas sensor. The new gas sensors based on Ga<sub>2</sub>O<sub>3</sub> films have very stable operating characteristics and are largely insensitive to humidity [14].

$\beta$ -Ga<sub>2</sub>O<sub>3</sub>, which exhibits some features like blue luminescence and ultraviolet emission [15, 16] implying the presence of grown oxygen vacancies as well as some impurities, stands as a very interesting candidate for having point defects and defect induced transport properties studied. However to study these properties, it is essential first to simulate the perfect crystal. One common approach for this is semiempirical atomistic simulation. Recently, a study of the energetics and migration of point defects in  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> has been reported, based on the shell model [17].

## 2. Structure and symmetry of $\beta$ -Ga<sub>2</sub>O<sub>3</sub>

Single crystals of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> can be grown by several techniques like the Verneuil technique, chemical transport method, vapour phase reaction method etc [18–21]. In spite of some



**Figure 1.** (a) Unit cell of  $\text{Ga}_2\text{O}_3$  with a view along the symmetry axis  $b$ . The solid spheres which are labelled with a star are halfway down the  $b$ -axis while others are in the plane of the paper. (b) Same unit cell with a view perpendicular to the symmetry axis  $b$ . Fractional coordinates are used for Ga and O ions.

debate [22], several investigations [23–25] on these crystals have shown that the crystal is monoclinic in structure with a space group of  $C2/m$ . There are four  $\text{Ga}_2\text{O}_3$  molecules per unit cell out of which two galliums ( $\text{Ga}_I$  and  $\text{Ga}_{II}$ ) and three oxygens ( $\text{O}_I$ ,  $\text{O}_{II}$  and  $\text{O}_{III}$ ) are crystallographically inequivalent to each other. An interesting feature of this structure is that the  $\text{Ga}^{3+}$  ions show two different coordinations in the unit cell.  $\text{Ga}_I$  ions are surrounded by tetrahedra each consisting of four oxygens while  $\text{Ga}_{II}$  are surrounded by octahedra each consisting of six oxygens. The oxygens on the other hand do not show any definite coordination. The cross sections of the unit cell along and perpendicular to the unique axis  $b$  are shown in figure 1.

The reported experimental values of the cell dimensions, fractional coordinates and average interionic distances [23] are listed in table 1. With the space group symmetry of  $C2/m$ , the multiplicity of each atom in the unit cell of  $\beta\text{-Ga}_2\text{O}_3$  is 8.

### 3. Perfect crystal calculations

Typically, for high symmetry ionic crystals, the pairwise potentials are Coulomb potentials and short range potentials. The short range potential parameters are taken to be independent variables and the structural parameters (cell parameters and ionic coordinates) are obtained by minimizing the lattice energy. During the process of minimization, the symmetries of the crystals are preserved. Bulk properties like the dielectric constant, elastic constants etc are then calculated for the optimized structure. The independent variables are varied in several loops until the computed bulk properties fit the experimental data.

In the case of low symmetry perfect crystals, induced ionic dipole moments are also present along with the monopoles. Since the electronic polarizabilities are not known *a priori*, we need to find these along with the potential parameters. In the MPPI model, the

**Table 1.** Experimental structural parameters for  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>.

(a) Cell parameters			
$a$ (Å)	$b$ (Å)	$c$ (Å)	$\beta$ (deg)
$12.23 \pm 0.02$	$3.04 \pm 0.01$	$5.80 \pm 0.01$	$103.7 \pm 0.3$
(b) Average interionic distances			
Ga-O		O-O	
Tetrahedral (Å)	Octahedral (Å)	Tetrahedron edge (Å)	Octahedron edge (Å)
1.83	2.00	3.02	2.84
(c) Fractional coordinates of the symmetry unique Ga and O ions in a unit cell			
Ion	$x$	$y$	$z$
Ga <sub>I</sub>	0.0904	0.0	-0.2052
Ga <sub>II</sub>	0.3414	0.0	-0.3143
O <sub>I</sub>	0.1674	0.0	0.1011
O <sub>II</sub>	0.4957	0.0	0.2553
O <sub>III</sub>	0.8279	0.0	0.4365

electronic polarizabilities are fitted to the static dielectric constant rather than high frequency dielectric constant. So we treat electronic polarizabilities as independent variables along with the potential parameters. However, designing a full fledged code to fit the short range potential parameters under MPPI model is beyond the scope of this work. We, therefore, split the problem into two steps.

In the first step, we find the short range potential parameters using a rigid ion model with the package GULP [7]. It has been shown in MPPI model calculations that the electronic polarizabilities are suppressed in the crystal environment and that their contribution to the total lattice energy is small [26]. It has also been shown that even with the TKS polarizabilities, the difference between the structural parameters with and without dipole moments is not very large [27]. On the basis of these findings, we suggest that the starting guess for potential parameters can be obtained by using a rigid ion calculation. The form of the potential is taken to be of Buckingham type:

$$\Phi(r) = A \exp\left(-\frac{r}{\rho}\right) - \frac{C}{r^6} \quad (1)$$

with  $A$ ,  $\rho$  and  $C$  as the strength, hardness and van der Waals parameters.

In the second step, we perform a full MPPI calculation in the presence of dipole moments and obtain electronic polarizabilities such that the computed properties fit well with the empirical data, like the static dielectric constant and structural parameters. An algorithm of these calculations is presented in figure 2.

### 3.1. Rigid ion calculations

GULP is primarily based on the shell model and is designed for both perfect and defect crystal calculations. However, it can be used for calculations based on the rigid model by eliminating the shells and putting the whole of the ionic charge at the core. Thus we get a system of non-polarizable ions which interact with each other via Coulomb and short range terms only.

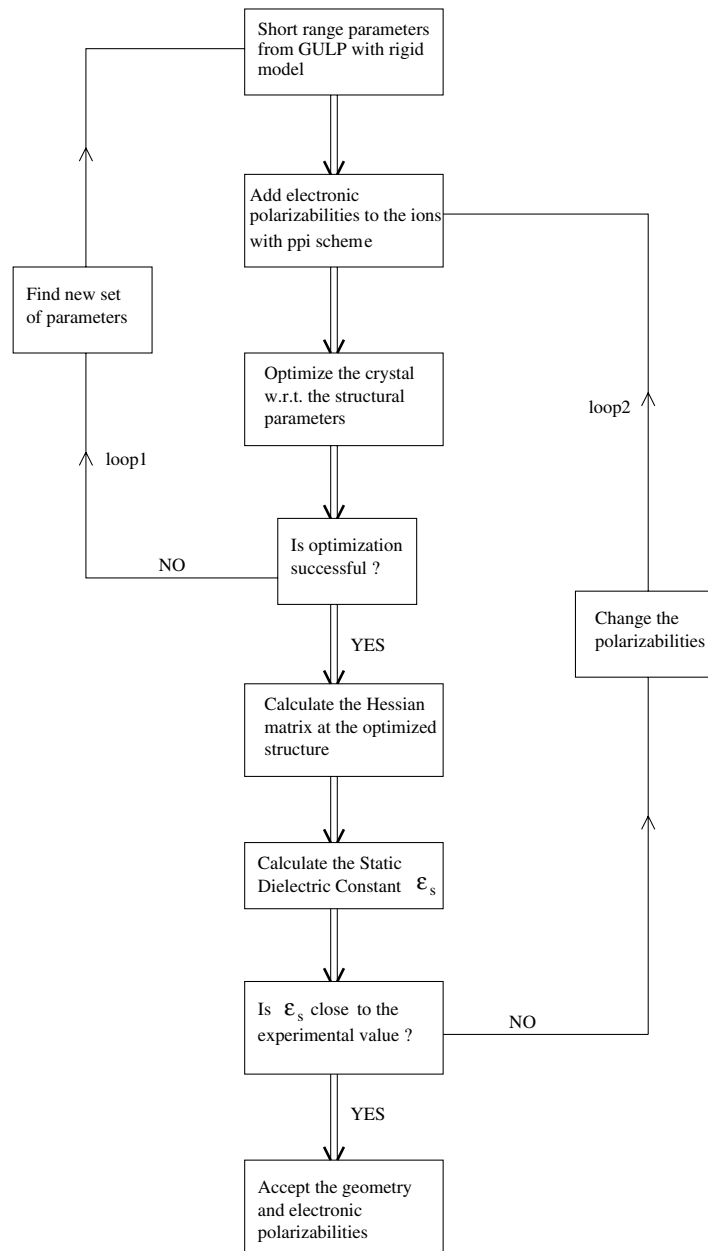


Figure 2. Algorithm for perfect crystal simulations.

In GULP, the relation between dielectric constant and the polarizability is given by

$$\epsilon_s = 1 + \frac{4\pi}{V_c} \alpha_d \quad (2)$$

where  $\epsilon_s$  is the static dielectric constant,  $\alpha_d$  is the displacement polarizability and  $V_c$  is the unit cell volume.

This relationship is based on Maxwell's field and neglects the local field correction. This is plausible, however, only for systems with low molecular concentration like in a gaseous medium where the polarization is also small and the local field becomes more or less the same as the average field [28]. On the other hand, for liquids and solids, the appropriate equation is the Clausius–Mossotti (CM) equation which has been derived taking into account the local field contributions:

$$\epsilon_s = \frac{1 + [8\pi/(3V_c)]\alpha}{1 - [4\pi/(3V_c)]\alpha}. \quad (3)$$

Here  $\alpha = \alpha_e + \alpha_d$  is the total polarizability, the sum of electronic ( $\alpha_e$ ) and displacement ( $\alpha_d$ ) polarizabilities.

This requires us to fit the rigid ion calculations to a lower value of dielectric constant. In addition, we can see from the CM relation that the dielectric constant is directly proportional to the polarizability. Our aim is to use the rigid model potential parameters in a MPPI model where the polarizability will be enhanced by contributions from the electronic part. Our initial guess is that the lower value of dielectric constant will be compensated by the addition of electronic polarizability. This is however not so straightforward, as the displacement polarizability will assume a new value in the MPPI scheme but still is expected to help in getting a good set of starting parameters for the MPPI calculations.

In GULP, the parameters were fitted at constant volume. Relax fitting was used, where at each point during the fit, the structure is optimized and the displacement of the structural parameters are calculated instead of the gradients.

### 3.2. MPPI calculations

The next step in the algorithm is to find optimal values of electronic polarizabilities by doing a full MPPI calculation. As discussed in the introduction section, the MPPI model was originally introduced and formulated to find the defect properties of ionic crystals with well established potential parameters derived either from *ab initio* calculation or empirical fitting. It was possible because all the MPPI calculations were done on high symmetry cubic crystals with the ions sitting at sites of zero electrostatic potential. However, this is not the case for low symmetry crystals and the MPPI scheme as such cannot be used.

The present work is the first attempt to reformulate the MPPI model and derive interatomic potentials in the low symmetry  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystal with this model. No attempt has yet been made to derive them with first-principles electronic structure calculation. Therefore, at present we cannot make any comparison of the MPPI with electronic structure calculations as far as potential parameters in this crystal are concerned. However, comparisons are possible in the case of  $\alpha$ -quartz [29] where derived *ab initio* potentials for Si–O and O–O compare well with previous empirical potentials. In the case of point defect calculations also, a good comparison has been shown between empirical and quantum mechanical procedures for MgO crystal [30].

Table 2 gives the net electric fields calculated at the experimental symmetry unique sites of the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> unit cell. Due to these non-zero electric fields and hence the dipole moments associated with the ions, we cannot neglect the contribution of polarization energy to the perfect lattice energy. In the MPPI calculations, we search for a stable structure by minimizing the lattice energy, only now, the dipole moments make the calculations more involved. The details of dipole moments, displacement polarizability, lattice energy and its gradient are given in the appendix.

With the potential parameters obtained from GULP, full MPPI calculation is repeated by varying the electronic polarizabilities until the experimental values are reproduced. However it

**Table 2.** Electric fields calculated at the experimental sites of symmetry unique ions in  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>.

	$E_x$ (eV Å <sup>-2</sup> )	$E_y$ (eV Å <sup>-2</sup> )	$E_z$ (eV Å <sup>-2</sup> )
Ga <sub>I</sub>	-0.306 689	0.0	-0.217 690
Ga <sub>II</sub>	-0.648 151	0.0	0.655 574
O <sub>I</sub>	4.781 664	0.0	0.136 894
O <sub>II</sub>	3.481 877	0.0	1.760 299
O <sub>III</sub>	1.637 611	0.0	1.700 481

**Table 3.** Short range potential parameters from the rigid ion model.

	$A$ (eV)	$\rho$ (Å)	$C$ (Å <sup>6</sup> )
Ga–O	246 171.374 421	0.166 441	145.768 417
O–O	664.800 374	0.542 162	57.096 413
Ga–Ga	45 240.235 760	0.266 733	0.513 166

may so happen that the optimization fails to converge to a stable structure. In this case, we go back to the rigid ion calculations to find a new set of potential parameters.

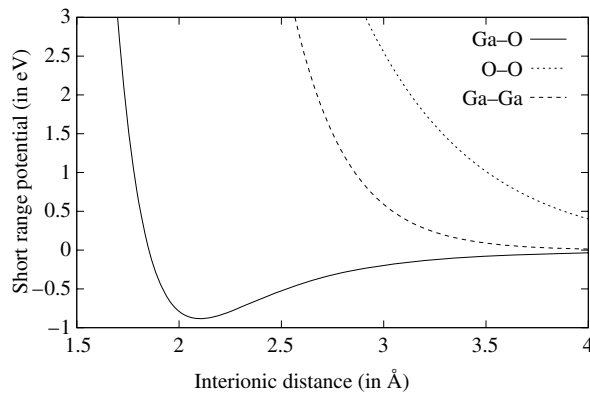
The optimization was done using the hsl (Harwell Subroutine Library) package va06. va06 calculates the least value of a multivariate function  $F(x_1, x_2, \dots, x_n)$  of  $n$  variables, where  $n \geq 2$ . The user has to provide an initial estimate of the required values of the variables  $(x_1, x_2, \dots, x_n)$  and a subroutine that calculates  $F(x_1, x_2, \dots, x_n)$  and the first derivatives  $\frac{\partial F}{\partial x_i}$ ,  $i = 1, 2, \dots, n$ , for any  $(x_1, x_2, \dots, x_n)$ . The energy gradient input makes the code work fast. The optimization technique used in this package is a combination of the steepest descent algorithm and the generalized Newton iteration. The Newton characteristics provide a fast final rate of convergence to the least value of the function and the steepest descent characteristics ensure a satisfactory accuracy criterion. The true minima are tested by finding the vibrational frequencies of the system. All of them are positive with the first three values null for the translational mode of the system.

#### 4. Results and discussion

After completing several iterations through loop 1 in the algorithm of figure 2, the final set of potential parameters from rigid ion calculations is given in table 3. The short range potential energies (for Ga–Ga, O–O and Ga–O) calculated with these parameters are plotted as a function of the interionic separation in figure 3. Within the nearest neighbour range (table 1), the O–O interaction dominates the other two owing to the larger size of the ions (average Shannon radii for tetrahedral and octahedral coordinations of Ga and O are 0.685 and 1.25 Å respectively). The structural parameters at this stage are shown in table 4 as taken from the output of GULP.

The dielectric constants in table 4 are derived from the Clausius–Mossotti relation. Electronic polarizabilities, both of gallium and oxygen, are varied independently to reproduce the experimental dielectric constant. For this, first we searched for stable structures of the crystal with respect to a coarse grid (step size 0.2) of the polarizabilities, the starting point being at (0, 0). It was observed that the process of optimization failed beyond the (1.4, 1.4) point (we say loop 1 fails when the optimization fails). The grid was then narrowed and made finer about the two approximate points ((0.2, 0.4) and (0.4, 0.2)) where the calculated dielectric constants were not far from the experimental value. The finer grid helped in estimating the two sets of polarizabilities, Set I and Set II, which gave the best comparison with the





**Figure 3.** Short range potential with fitted parameters for Ga–O, O–O and Ga–Ga plotted as a function of interionic distance.

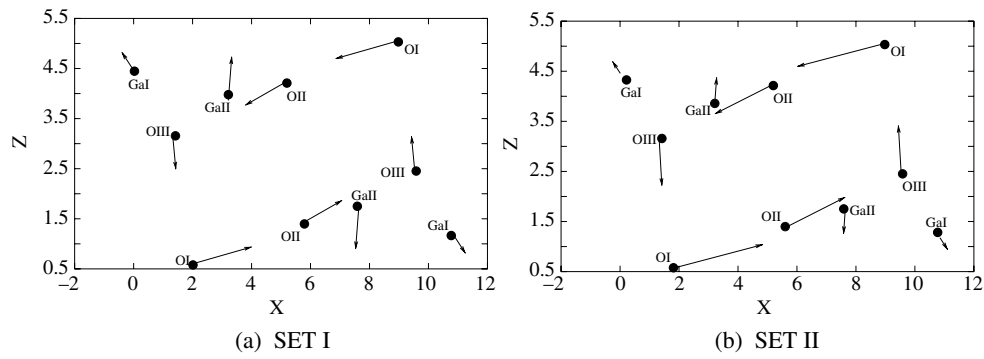
**Table 4.** Fitted parameters from GULP.

(a) Structural			
Lattice energy (eV)		–500.99	
		<i>x</i>	<i>z</i>
Position (functional)	Ga <sub>I</sub>	0.0896	0.7909
	Ga <sub>II</sub>	0.3397	0.6853
	O <sub>I</sub>	0.1651	0.1030
	O <sub>II</sub>	0.4972	0.2515
	O <sub>III</sub>	0.8285	0.4364
(b) Dielectric			
	Input	Calculated	
Static dielectric constant	5.32	5.36	

**Table 5.** Fitted values of the static dielectric constant and polarizabilities with the MPPI scheme.

	Dielectric constant		Polarizability		
	Experimental	Calculated	Anion ( $\text{\AA}^3$ )	Cation ( $\text{\AA}^3$ )	Displacement per unit cell ( $\text{\AA}^3$ )
Set I	10.2	10.29	0.25	0.458	33.84
Set II	10.2	10.16	0.35	0.250	33.99

experimental value. The fitted electronic polarizabilities along with the calculated displacement polarizabilities and dielectric constants are listed in table 5. As expected within the MPPI scheme, the calculated electronic polarizabilities are much lowered as compared to the free ion values ( $\alpha_{\text{Ga}} = 1.5 \text{ \AA}^3$ ,  $\alpha_{\text{O}} = 2.01 \text{ \AA}^3$ ) [31]. The displacement polarizability is actually a  $3 \times 3$  matrix. We neglect the anisotropic effect as it is very small and take the average of the diagonal elements to be the approximate scalar displacement polarizability. Table 6 gives the final values of structural parameters along with their deviations from the experimental values



**Figure 4.** Vector plot of dipole moments for the (010) plane of the unit cell. Cartesian coordinates are used for Ga and O ions.

**Table 6.** Structural parameters after MPPI simulation. The delta values give the deviation of the respective quantities from their experimental values.

(a) Set I					
Lattice energy (eV)		-501.642			
		$x$	$\delta x$	$z$	$\delta z$
Position (fractional)	Ga <sub>I</sub>	0.089 575	0.000 825	0.791 027	0.003 773
	Ga <sub>II</sub>	0.339 707	0.001 693	0.685 384	0.000 316
	O <sub>I</sub>	0.165 167	0.002 233	0.103 006	-0.001 906
	O <sub>II</sub>	0.497 140	-0.001 440	0.251 485	0.003 815
	O <sub>III</sub>	0.828 538	-0.000 638	0.436 339	0.000 161
(b) Set II					
Lattice energy (eV)		-501.806			
		$x$	$\delta x$	$z$	$\delta z$
Position (fractional)	Ga <sub>I</sub>	0.089 536	0.000 864	0.791 143	0.003 657
	Ga <sub>II</sub>	0.339 725	0.001 675	0.685 523	0.000 177
	O <sub>I</sub>	0.165 284	0.002 116	0.103 009	-0.001 909
	O <sub>II</sub>	0.497 088	-0.001 388	0.251 548	0.003 752
	O <sub>III</sub>	0.828 523	-0.000 623	0.436 299	0.000 201

for both sets of polarizabilities. From the table we can see that the potential parameters and the polarizabilities have been closely fitted to the experimental structure.

In semiempirical calculations, the choices of potentials and polarizabilities are not unique. They are to be evolved so as to best fit the experimental data and reproduce the materials properties. Electronic polarizabilities of ions depend on their site potentials in a low symmetry crystal. In a crystal like  $\text{Ga}_2\text{O}_3$  where the constituent ions are heavily charged ( $\text{Ga}^{3+}$ ,  $\text{O}^{2-}$ ), little changes in the positions of the ions cause considerable changes in the electrostatic potential and hence polarizabilities of individual ions. However, the total polarizability of the cell (electronic + displacement) remains nearly the same and hence so does the dielectric constant. Owing to this, the bulk properties of the crystal, as we have seen in the case of lattice energy, will not be affected considerably for the two sets of polarizabilities that are presented here. Variation in the values of oxygen and gallium polarizabilities are expected to become significant in any further calculation of defect parameters. Each of the ions will then

**Table 7.** Electric fields and dipole moments at symmetry unique ions.

(a) Set I				
	Electric field ( $e^2 \text{ \AA}^{-2}$ )		Dipole moment ( $e \text{ \AA}$ )	
	<i>x</i> -component	<i>z</i> -component	<i>x</i> -component	<i>z</i> -component
Ga <sub>I</sub>	-0.017 666	0.021 214	-0.013 494	0.012 161
Ga <sub>II</sub>	0.009 381	0.056 758	0.003 771	0.029 015
O <sub>I</sub>	0.278 301	0.052 550	0.070 729	0.011 887
O <sub>II</sub>	0.176 177	0.058 606	0.044 325	0.014 959
O <sub>III</sub>	-0.024 107	0.087 750	-0.003 674	0.022 822

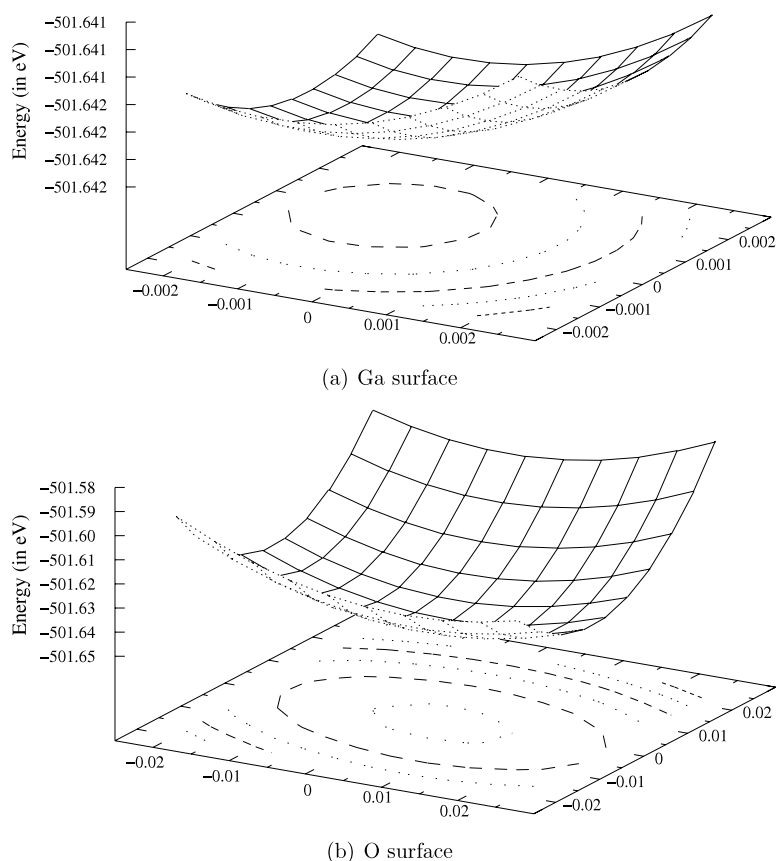
(b) Set II				
	Electric field ( $e^2 \text{ \AA}^{-2}$ )		Dipole moment ( $e \text{ \AA}$ )	
	<i>x</i> -component	<i>z</i> -component	<i>x</i> -component	<i>z</i> -component
Ga <sub>I</sub>	-0.016 434	0.020 033	-0.008 699	0.007 892
Ga <sub>II</sub>	0.007 663	0.055 515	0.002 061	0.017 069
O <sub>I</sub>	0.281 236	0.052 6475	0.098 620	0.015 277
O <sub>II</sub>	0.175 750	0.061 230	0.063 283	0.018 862
O <sub>III</sub>	-0.024 143	0.087 040	-0.003 172	0.031 9074

**Table 8.** Phonon frequencies (from Set I).

Mode	Freq. (cm <sup>-1</sup> )	Mode	Freq. (cm <sup>-1</sup> )	Mode	Freq. (cm <sup>-1</sup> )	Mode	Freq. (cm <sup>-1</sup> )
1	9.51	16	374.66	31	685.98	46	1364.24
2	2.44	17	472.07	32	700.30	47	1414.24
3	7.15	18	475.37	33	715.34	48	1422.42
4	156.31	19	476.32	34	760.84	49	1429.25
5	175.64	20	484.83	35	767.19	50	1429.37
6	175.84	21	485.51	36	768.25	51	1433.78
7	195.44	22	497.33	37	847.60	52	1461.28
8	229.06	23	506.02	38	849.40	53	1461.71
9	237.25	24	520.74	39	901.44	54	1473.33
10	252.07	25	524.23	40	1095.46	55	1550.95
11	292.07	26	584.09	41	1114.50	56	1590.08
12	313.18	27	628.91	42	1205.60	57	1710.46
13	329.92	28	630.90	43	1208.69	58	1764.77
14	359.65	29	668.42	44	1223.77	59	1766.21
15	363.12	30	670.59	45	1326.47	60	1792.18

be experiencing large electrostatic fields and the polarization energy will play an important role in the convergence of defect parameters.

Table 7 gives the net electric field and dipole moments of the symmetry unique ions in the crystal for the optimized structure. It is observed that the electric fields at individual ion sites are considerably suppressed in the MPPI scheme as compared to those from table 2 for the experimental structure. Vector plots of the dipole moments for both Set I and Set II are presented for a single unit cell in figure 4. We see here that with increasing polarizabilities, the dipole moments of the oxygens increase in Set II as compared to Set I. The reverse is the case for galliums.



**Figure 5.** Optimized energy surfaces showing minima for arbitrarily chosen Ga and O ion coordinates from Set I. The Ga surface here is obtained by varying the  $x$ -coordinate of Ga at (0.089, 0.0, 0.79) with respect to the  $x$ -coordinate of Ga at (0.91, 0.0, 0.21), whereas the O surface is obtained by varying the  $x$ -coordinate of O at (0.16, 0.0, 0.10) with respect to the  $z$ -coordinate of the same ion. The actual minima lie in a 60-dimensional space defined by 20 ions in the unit cell of the crystal.

Figures 5(a) and (b) show the minima of Ga and O energy surfaces in two dimensions. These surfaces correspond to Set I polarizabilities. Phonon frequencies have been calculated from the mass weighted Hessian matrix for both the sets. We list here only those from Set I in table 8. We observe that the first three values in both the cases are sufficiently small in comparison to the other values. Actually, these small values are due to computer round-off error propagating from the Hessian matrix and eigenvalue calculations. They can be approximated to zero representing the three translational modes of the system. The positive definite values of all the other modes confirm the stability of the crystal at the particular structure.

## 5. Conclusions

We have studied the two-body interionic interactions in a perfect crystal of very low symmetry using the MPPI model. The present work which finds a set of potential parameters and electronic polarizabilities for the low symmetry  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> will initiate further work in this field. The optimized parameters along with the electronic polarizabilities can now be used for

various point defect calculations for this material within the dipolar approximation. Moreover, taking these parameters as the initial ones, the present calculations can be extended to include quadrupole polarizabilities based on the EPPI scheme. We believe that, for a low symmetry crystal, there will be substantial contributions from the quadrupoles to the perfect crystal parameters. This will in turn affect the thermodynamics of the defect crystal.

## Appendix

### Induced dipole moments

Neglecting the higher order moments, the exact equation for solving for the dipole moment of an ion at site  $i$  is

$$\boldsymbol{\mu}_i = \alpha_{e,i} (\mathbf{F}_i^m + \mathbf{F}_i^d) \quad (\text{A.1})$$

where  $\alpha_{e,i}$  is the electronic polarizability and  $\mathbf{F}_i^m$ ,  $\mathbf{F}_i^d$  are the total monopole and dipole fields acting on the ion sitting at the  $i$ th site.

Equation (A.1) can be written in matrix form as

$$\sum_j \sum_\beta D_{ij}^{\alpha\beta} \mu_j^\beta = M_i^\alpha, \quad M_i^\alpha = \alpha_{e,i} F_i^{m,\alpha} \quad (\text{A.2})$$

where

$$D_{ij}^{\alpha\beta} = \delta_{\alpha\beta} + \sum_l \left( -3\alpha_{e,i} \frac{r^\alpha r^\beta}{r^5} + \alpha_{e,i} \frac{\delta_{\alpha\beta}}{r^3} \right) \quad i = j. \quad (\text{A.3})$$

$$= \sum_l \left( -3\alpha_{e,i} \frac{r^\alpha r^\beta}{r^5} + \alpha_{e,i} \frac{\delta_{\alpha\beta}}{r^3} \right) \quad i \neq j. \quad (\text{A.4})$$

The term  $M_i^\alpha$  involving the monopole field is calculated using Ewald's method [32]. Here,  $\alpha$ ,  $\beta$  are the Cartesian coordinates.

We now have dipolar forces at individual ion sites owing to the dipoles of all other ions. The inclusion of this dipolar force has the effect of changing the displacement polarizability of individual ions and changing the net lattice energy to be discussed below.

### Displacement polarizability

With a uniform external electric field  $\mathbf{F}_{\text{ext}}$  acting on it, the lattice energy of a perfect crystal in the presence of dipole moments of individual ions can be written as

$$E = E_0 + \frac{1}{2} \boldsymbol{\xi}^T \mathbf{W} \boldsymbol{\xi} - q^T (\boldsymbol{\xi} \cdot \mathbf{F}_{\text{ext}}) - \boldsymbol{\mu} \cdot \mathbf{F}_{\text{ext}}. \quad (\text{A.5})$$

If there are  $s$  ions in one unit cell,  $\boldsymbol{\xi}$  is a  $3s$ -dimensional vector of displacements,  $q$  is an  $s$ -dimensional array of charges,  $\boldsymbol{\mu}$  is the  $3s$ -dimensional vector of ionic dipole moments and  $\mathbf{W}$  is the  $3s \times 3s$  force constant matrix.  $E_0$  is the lattice energy in the absence of the external field.

Using the equilibrium condition to get the displacement, the displacement polarizability of the  $i$ th ion in the component form comes out to be

$$\alpha_{d,i}^{\alpha\beta} = q_i \sum_j [\mathbf{W}^{-1}]_{ij}^{\alpha\beta} \left\{ q + \sum_\gamma (\delta \mu_\gamma)^\beta \right\}. \quad (\text{A.6})$$

Here, the indices  $i$  and  $j$  go over the  $(s - 1)$  unit cell ions.

*Lattice energy*

The lattice energy  $E_L$  of a perfect ionic crystal can be straightaway divided into two parts—the long range electrostatic part and the short range overlap repulsion as well as the van der Waals part.

In the absence of any induced dipole moments, the electrostatic energy of a system of ions can be written simply as the sum of monopole and dipole terms. However if the ions are close enough to influence each other, they will induce polarization in the neighbouring ions. In that case, we need to take care of the dipole self-energy term also.

So, the total electrostatic energy of a crystal with polarizable point ions comes out to be

$$E^{ES} = E^{mm} + E^{dm} + E^{md} + E^{dd} + E^{self}, \quad (A.7)$$

where  $E^{mm}$  is the monopole–monopole interaction energy,  $E^{dm}$  and  $E^{md}$  are the monopole–dipole interaction energies, and  $E^{dd}$  is the dipole–dipole interaction energy. The last term  $E^{self}$  is the self-energy of formation of the induced dipole moments.

When taking the explicit expressions, the dipole–dipole term plus half of the monopole–monopole term gets cancelled with the self-energy term and we are left with

$$E^{ES} = E^{mm} - \frac{1}{2}E^{md}. \quad (A.8)$$

As for the short range term, the sum is terminated at some reasonable cut-off limit. It is essential to evaluate the electrostatic Coulomb term with much care and attention as it is the dominant term for oxides. We have evaluated this term using Ewald’s method [32].

*Gradient of the lattice energy*

The availability of the first derivative of the energy is useful in the minimization of the energy. The effort in this case lies entirely in finding the gradient of the dipole moment associated with the monopole–dipole energy. This is because the dipole moments are in turn associated with the different field terms of the system through a set of linear equations.

The simple derivative terms of the monopole and short range energies are

$$\delta E^{mm} = \sum_i q_i F_i^m \quad (A.9)$$

and

$$\delta E^{SR} = \sum_i \sum_j \left\{ -\frac{1}{\rho_{ij}} A_{ij} \exp\left(-\frac{r}{\rho_{ij}}\right) + \frac{6C_{ij}}{r^7} \right\}. \quad (A.10)$$

For  $E^{md}$  term we start with the derivative of  $E^{md}$  with respect to  $r_k^\gamma$ :

$$\delta_k^\gamma E^{md} = -\frac{1}{2} \sum_{i,\alpha} \{ (\delta_k^\gamma \mu_{i,\alpha}) F_i^{m,\alpha} + \mu_{i,\alpha} (\delta_k^\gamma F_i^{m,\alpha}) \}. \quad (A.11)$$

Taking the derivative of  $\mu_i^\alpha$  from equation (A.2):

$$\delta_k^\gamma \mu_i^\alpha = \sum_{j,\beta} (D^{-1})_{ij}^{\alpha\beta} (\delta_k^\gamma F^m)_j^\beta - \sum_{l,\delta} \sum_{j,\beta} (D^{-1})_{il}^{\alpha\delta} (\delta_k^\gamma D)_{lj}^{\delta\beta} \mu_j^\beta, \quad (A.12)$$

where the derivative of  $D$  is

$$\delta_k^\gamma D_{ij}^{\alpha\beta} = \begin{cases} 0 & i = j \\ 0 & k \neq i, k \neq j \\ \sum_l \frac{\alpha_i}{r^7} (15r^\alpha r^\beta r^\gamma - 3r^2 (r^\alpha \delta_{\beta\gamma} + r^\beta \delta_{\alpha\gamma} + r^\gamma \delta_{\alpha\beta})) & k = i, k \neq j \\ \sum_l -\frac{\alpha_i}{r^7} (15r^\alpha r^\beta r^\gamma - 3r^2 (r^\alpha \delta_{\beta\gamma} + r^\beta \delta_{\alpha\gamma} + r^\gamma \delta_{\alpha\beta})) & k = j, k \neq i. \end{cases} \quad (A.13)$$

We now define a function  $U_{ij}^{\alpha\beta\gamma}$  such that

$$\delta_k^\gamma D_{ij}^{\alpha\beta} = U_{ij}^{\alpha\beta\gamma} \delta_{kj} - U_{ij}^{\alpha\beta\gamma} \delta_{ki}. \quad (\text{A.14})$$

So

$$U_{ij}^{\alpha\beta\gamma} = \begin{cases} 0 & i = j \\ \sum_l \frac{\alpha_l}{r^7} (15r^\alpha r^\beta r^\gamma - 3r^2 (r^\alpha \delta_{\beta\gamma} + r^\beta \delta_{\alpha\gamma} + r^\gamma \delta_{\alpha\beta})) & i \neq j. \end{cases} \quad (\text{A.15})$$

$U_{ij}^{\alpha\beta\gamma}$  is symmetric under permutations of  $\alpha, \beta, \gamma$  and that of  $i$  and  $j$ .

The derivative of  $F_i^m$  is

$$\delta_k^\gamma F_i^{m,\alpha} = \begin{cases} -\alpha_i \left[ \sum_l q_j \left( \frac{\partial f_1(r)}{\partial r} \frac{r^\alpha r^\gamma}{r^2} + f_1(r) \left( \delta_{\alpha\beta} \frac{1}{r} - \frac{r^\alpha r^\gamma}{r} \right) \right) \right]_{r \neq 0} \\ \quad + \frac{4\pi q_j}{V_c} \sum_{G \neq 0} f_2(G) G_\alpha G_\gamma \cos(\mathbf{G} \cdot \mathbf{r}) & k \neq i \\ \alpha_i \left[ \sum_l \sum_j q_j \left( \frac{\partial f_1(r)}{\partial r} \frac{r^\alpha r^\gamma}{r^2} + f_1(r) \left( \delta_{\alpha\beta} \frac{1}{r} - \frac{r^\alpha r^\gamma}{r} \right) \right) \right]_{r \neq 0} \\ \quad + \sum_j \frac{4\pi q_j}{V_c} \sum_{G \neq 0} f_2(G) G_\alpha G_\gamma \cos(\mathbf{G} \cdot \mathbf{r}) & k = i \end{cases} \quad (\text{A.16})$$

where

$$\frac{\partial f_1(r)}{\partial r} = \frac{4}{\sqrt{\pi}} g \left( g^2 + \frac{1}{r^2} \right) e^{-g^2 r^2} + \frac{2}{r^3} \text{erfc}(gr).$$

Putting  $\delta_k^\gamma \mu$  and  $\delta_k^\gamma F^m$  in equation (A.11), we get  $\delta_k^\gamma E^{\text{md}}$  and so the total derivative term is

$$\delta E^{\text{md}} = \sum_{k,\gamma} \delta_k^\gamma E^{\text{md}}. \quad (\text{A.17})$$

### The second derivative or the Hessian matrix of energy

It is essential to calculate the second derivative or Hessian matrix of the energy to get the static dielectric constant property of the crystal. Moreover, the positive definiteness of the Hessian matrix ensures a true minimum of the multivariate system.

The second derivative of energy is easy and straightforward to calculate only when the ions in the perfect environment are at electrostatically neutral positions when there are only monopole and short range terms. As soon as the dipole term comes into the picture, it involves a calculation of second derivative of the dipole moment which is rather complicated and expensive. In that case, it is more viable to go for numerical calculation of the Hessian matrix rather than an analytical one.

Let  $f(x_1, \dots, x_i, \dots, x_j, \dots, x_s)$  be the energy function, where  $x_1, x_2, \dots, x_s$  are the relaxations of the unit cell ions. Then using Stirling's formula [33], the first derivative of the function  $f(x_1, \dots, x_i, \dots, x_j, \dots, x_s)$  w.r.t.  $x_i$  can be written as

$$\frac{\partial f}{\partial x_i} = \frac{f(x_1, \dots, x_i + h, \dots, x_n) - f(x_1, \dots, x_i - h, \dots, x_n)}{2h}. \quad (\text{A.18})$$

This formula can be extended to get the second derivative of energy as

$$\frac{\partial^2 f}{\partial x_i \partial x_j} = \frac{1}{4h^2} (f_1 - f_2 - f_3 - f_4). \quad (\text{A.19})$$

Here,

$$f1 = f(x_1, \dots, x_i + h, \dots, x_j + h, \dots, x_n).$$

$$f2 = f(x_1, \dots, x_i + h, \dots, x_j - h, \dots, x_n).$$

$$f3 = f(x_1, \dots, x_i - h, \dots, x_j + h, \dots, x_n).$$

$$f4 = f(x_1, \dots, x_i - h, \dots, x_j - h, \dots, x_n).$$

## References

- [1] Dick B G and Overhauser A W 1958 *Phys. Rev.* **112** 90
- [2] Mott N F and Littleton M J 1938 *Trans. Faraday Soc.* **34** 485
- [3] Murti Y V G S and Usha V 1976 *Physica B* **83** 275
- [4] Banhatti R D and Murti Y V G S 1993 *Phys. Rev. B* **48** 6839–53
- [5] Sahariah M B, Banhatti R D, Kadolkar C Y and Murti Y V G S 1999 *Indian J. Pure Appl. Phys.* **37** 306
- [6] Sahariah M B 2005 *PhD Thesis* IIT Guwahati
- [7] Gale J D 1997 Gulp: a computer program for the symmetry adapted simulation of solids *J. Chem. Soc. Faraday Trans.* **93** 629–37
- [8] Norgett M J 1974 A general formulation of the problem of calculating the energies of lattice defects in ionic crystals *AERE Report AERE-R. 7650* (United Kingdom Atomic Energy Authority) p 49
- [9] Edwards D P 1998 Beta-gallium oxide *Handbook of Optical Constants of Solids III* (San Diego, CA: Academic Press) p 753
- [10] Ueda N and Hosono H 1997 *Appl. Phys. Lett.* **70** 3561
- [11] Palik E D, Ginsburg N, Holm R T and Gibson J W 1978 *J. Vac. Sci. Technol.* **15** 1488
- [12] Peter M and Schawlow A L 1960 *Bull. Am. Phys. Soc. II* **5** 158
- [13] Ueda N, Hosono H, Waseda R and Kawazoe H 1997 *Appl. Phys. Lett.* **71** 933
- [14] Bernhardt K, Fleischer M and Meixner H 1995 *Siemens Compon.* **30** 35
- [15] Harwig T, Kellendonk F and Slappendal F 1978 *J. Phys. Chem. Solids* **39** 675–80
- [16] Binet L and Gourier D 1998 *J. Phys. Chem. Solids* **59** 1241–9
- [17] Blanco M A, Sahariah M B, Jiang H, Costales A and Pandey R 2005 *Phys. Rev. B* **72** 184103
- [18] Remeika J P 1960 *J. Appl. Phys.* **31** 263S
- [19] Chase A B 1964 *J. Am. Ceram. Soc.* **47** 470
- [20] Matsumoto T, Aoki M, Kinoshita A and Aono T 1974 *Japan. J. Appl. Phys.* **13** 737  
Matsumoto T, Aoki M, Kinoshita A and Aono T 1974 *Japan. J. Appl. Phys.* **13** 1578
- [21] Juskowiak H and Pajczkowska A 1986 *J. Mater. Sci.* **21** 3430
- [22] Wolten G M and Chase A B 1976 *J. Solid State Chem.* **16** 377–83
- [23] Geller S 1960 *J. Chem. Phys.* **33** 676
- [24] Geller S 1977 *J. Solid State Chem.* **20** 209
- [25] Ahman J, Svensson G and Albertsson J 1996 *Acta Crystallogr. C* **52** 1336–8
- [26] Banhatti R D 1993 *PhD Thesis* IIT Madras
- [27] Doye J P K and Wales D J 1998 *Preprint cond-mat/9801152*
- [28] Omar M A 1999 *Elementary Solid State Physics* (Singapore: Pearson Education)
- [29] Parton J, Jones R, Catlow C R A and Leslie M 1993 *Phys. Chem. Minerals* **19** 392–400
- [30] Grimes R W, Catlow C R A and Stoneham A M 1989 *J. Phys.: Condens. Matter* **1** 7367–84
- [31] Grimes N W and Grimes R W 1997 *J. Phys.: Condens. Matter* **9** 6737–47
- [32] Dove M T 1993 *Introduction to Lattice Dynamics* (Cambridge: Cambridge University Press)
- [33] Hildebrand F B 1987 *Introduction to Numerical Analysis* (New York: Dover Publications)