

Density-functional theory for the energy of crystals: Test of the ionic model

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A test of the ionic description of bonding is made for a wide variety of crystals. Self-consistent Hartree-Fock calculations provide the charge densities of the ions, from which the crystal energy is evaluated with a modified electron-gas energy functional. Thus, the crystal binding energy is found by *a priori* quantum-mechanical methods without fitting any adjustable parameters to experimental data. The theoretical crystal energies are minimized by varying the geometry of the crystals to predict the stable structures and equilibrium energies of the crystals. For the more highly ionic crystals, in which the electronegativity difference between atoms is *larger* than about one, this purely ionic theory predicts both crystal geometry and binding energy to an average accuracy of $\pm 2\%$. For less ionic crystals, with electronegativity differences less than about one, the purely ionic theory gives larger errors, as expected, ranging up to about 8%. We conclude that the ionic description of bonding is quite accurate for a surprisingly wide range of crystals.

I. INTRODUCTION

Since the first applications of quantum mechanics to chemistry, many of our basic ideas about chemical bonding have focused on the covalent bond. The earliest calculations¹ on H_2^+ and H_2 gave remarkable explanations for molecular bonding, and Pauling,² using empirical arguments, extended these ideas to many-electron molecules. From the electronegativity scale of the elements, he explained almost all chemical bonding in terms of distortions from the pure covalent bonds found in homonuclear molecules. In this scheme the fully ionic bond appears as an extreme limiting case, observable only in very few molecules, such as the alkali halides.

Although the bonding in nonmetallic solids should not be fundamentally different from molecular bonding, most theories of crystals have used an ionic description of the bonding where at all possible, and a large variety of crystalline compounds have been treated by semiempirical theories assuming a crystal comprised of ionic units. In addition to numerous applications of this type to alkali halides,^{3,4} calculations on less ionic compounds such as oxides and sulfides have been reported.⁵⁻⁷ Ionic models of crystals have been adopted mainly for practical convenience, however, with little *a priori* theoretical justification. Failures of ionic models have traditionally been attributed to covalent effects, but no independent assessment of the validity of ionic models has been possible because of the many adjustable empirical parameters which are fitted to the very crystal properties (binding energy, lattice constant, etc.) which would best test the models.

Recently, we⁸ presented an *ab initio* electron-gas theory for crystals, also based on a fully ionic description of the bonding. The methods presented were sufficiently general to allow their

application to a wide variety of crystals. Since no empirical results are required by the theory, it can be applied to many systems for which experimental results are lacking, such as crystals at extremes of high pressure and temperature. In our previous paper we gave results for a number of highly ionic systems where the electronegativity differences^{2,9} between the component species were in the range $|\Delta\chi|=2.0-3.0$. Differences between theoretical and experimental geometries and dissociation energies were only on the order of 1-3%, and there was no discernible correlation of the errors with electronegativity difference. The question thus arises of how generally applicable the electron-gas theory and the ionic models of crystal bonding are to crystals with smaller electronegativity differences.

In this paper we present results for many additional crystals, including some with very small electronegativity differences, in order to further evaluate the utility of the model and test its limits of applicability. Since dipolar distortions of the ions are not considered in the present version of the theory, we confine ourselves to systems of relatively high site symmetry. In the next section the electron-gas crystal theory is briefly reviewed. In Sec. III theoretical results for equilibrium geometries and dissociation energies in alkali chlorides are presented. The agreement between theory and experiment for these systems is excellent. In addition, we consider the relative stabilities of the *B1* (fcc), *B2* (bcc) and *B3* (sphalerite) structures for these systems. As we found previously,⁸ the model tends to predict slightly excessive stability of the *B3* phase over the *B1* and the *B1* over the *B2*. Since the beryllium, magnesium, and calcium chlorides are found in rather distorted structures, we have not applied the theory to them. In Sec. IV, however, we present the first electron-gas results for SrF_2

and SrCl_2 , which have the more symmetric fluorite structure. The stability of a rutile form of these compounds is also examined.

In the remaining sections of the paper, applications to increasingly-less-ionic systems are presented. Our results for a number of oxide crystals, not previously treated by electron-gas calculations, are in Sec. V. In addition to BeO and SrO , we examine SiO_2 in its high cristobalite modification, which is its most symmetric form, and CaTiO_3 and CaSiO_3 in the cubic perovskite lattice. Results for KAlO_2 are also included in this section. For these oxides we find no indications of a breakdown of the theory. The calculated equilibrium geometries and dissociation energies of the alkali and alkaline-earth sulfides are given in Sec. VI. Although the electronegativity differences between the elements in these systems fall in the range of 1.0–2.0, the calculated results for all but BeS are within four percent of the experimental values, with average errors of about two percent. Calculations on the alkali hydrides and MgH_2 were also performed. In Sec. VII we show that the results for these systems using the Waldman-Gordon combination rules for correction factors¹⁰ display large and systematic errors. We propose an alternate set of combining rules for the correction factors for hydrides, which give errors comparable to those for the systems considered previously. In Sec. VIII we show how the theory may be applied to nitride crystals assuming the existence of the N^{3-} ion in these compounds. We obtain good results for Be_3N_2 , AlN , and ScN , but find larger errors in the dissociation energies for Li_3N and BN . Proceeding to even smaller electronegativity differences, we treat AlP , Be_2C , and SiC as ionic crystals in Sec. IX. Here we see a clear breakdown of the model in that the calculated lattice constants for these systems are significantly ($\approx 7\%$) smaller than the experimental values. We interpret these errors as a failure of the ionic charge distribution to describe these crystals. In the actual crystals the binding apparently occurs with a significant shift of electron density from the anions towards the internuclear bonding regions leading to larger nearest-neighbor distances than those calculated from a purely ionic theory. For electronegativity differences larger than unity ($|\Delta\chi| > 1.0$), the model generally gives both the geometry and dissociation energy to within four percent of the experimental values with average errors of 1–3%. For electronegativity differences less than unity ($|\Delta\chi| \leq 1.0$), the error in at least one of these quantities is fairly large (up to about 8%). A more complete discussion of the overall results is found in Sec. X.

II. REVIEW OF THEORY

In this section we will briefly describe the theory used to calculate crystal geometries and dissociation energies. Complete details are given in Ref. 8. We assume that the total charge density in the crystal can be written as a superposition of the densities of the individual ionic components of the crystal, or

$$\rho_T(\vec{x}) = \sum_i \sum_{\vec{r}_{i1}} Z_i \delta(\vec{x} - \vec{r}_{i1}) - \rho_i(\vec{x} - \vec{r}_{i1}), \quad (1)$$

where $\rho_i(\vec{x} - \vec{r}_{i1})$ is the electronic density of ion i centered at \vec{r}_{i1} and Z_i is the nuclear charge. We sum over the ions in a unit cell and all the direct-lattice vectors. The binding energy of the crystal W_B is defined to be the crystal interaction energy per formula unit relative to the fixed charge densities $Z_i \delta(\vec{x}) - \rho_i(\vec{x})$ at infinite separation, and is split into electrostatic, exchange, kinetic, and correlation components. The latter three are obtained from the energy density functionals of the electron gas theory,¹¹ and for crystals may be obtained by integrating

$$W = \int_V d\vec{x} \mathcal{E} \left(\sum_i \sum_{\vec{r}_{i1}} \rho_i(\vec{x} - \vec{r}_{i1}) \right) - \sum_i \sum_{\vec{r}_{i1}} \mathcal{E}[\rho_i(\vec{x} - \vec{r}_{i1})] \quad (2)$$

over a unit cell of the crystal. Each of the electron-gas energy terms is found in this manner, with $\mathcal{E}[\rho(x)]$ the appropriate energy density functional. Equation (2) gives the interaction energy directly and includes nonlinear many-body effects due to the simultaneous overlap of three or more charge distributions.

The electrostatic interaction energy is given by

$$W_E = \frac{1}{2} \int d\vec{x} \sum_i [Z_i \delta(\vec{x} - \vec{r}_i) - \rho_i(\vec{x} - \vec{r}_i)] \Phi_i(\vec{x}), \quad (3)$$

where

$$\Phi_i(\vec{x}) = \int d\vec{y} [\rho_T(\vec{y}) - Z_i \delta(\vec{y} - \vec{r}_i) + \rho_i(\vec{y} - \vec{r}_i)] / |\vec{x} - \vec{y}|. \quad (4)$$

This term cannot be calculated directly from Eq. (3) and instead was split up into terms involving the Madelung energy, a direct and a reciprocal-lattice summation, a three-dimensional numerical integration, and terms resembling self-energies of the charge distributions. This allowed for rapid and efficient evaluation of all components of the interaction energy.

The electronic charge densities $\rho_i(\vec{x})$ are determined from atomic Hartree-Fock self-consistent-field (SCF) wave functions. The stabilizing effect

of the crystal potential on these ionic densities was approximated by including a spherical shell potential in the atomic Hamiltonian. The charge on the shell was chosen to be the negative of the ionic charge and the overall method was made self-consistent by choosing the shell radius r_0 , such that the shell potential matched the crystal site potential at each ion. This resulted in a net contraction of the anion density but had a negligible effect on the cation. This procedure led to significantly better results than those obtained with gas-phase or partially stabilized wave functions. Since the spherical symmetry of the ions was preserved, the model remains fully ionic, with no charge transfer between ions.

The binding energy, calculated from the shell-stabilized (SS) wave functions, then refers to the infinitely separated stabilized ions and not experimentally observable gaseous anions or neutral species. The dissociation energy D_e of the crystal into free cations and singly charged anions is obtained theoretically from the binding energy and differences in energy between the SS ions and the free anions. This dissociation energy may also be calculated entirely from experimental results so that a meaningful comparison between theoretical and experimental dissociation energies can be made.

III. EQUILIBRIUM GEOMETRIES AND DISSOCIATION ENERGIES FOR ALKALI CHLORIDES

There is a great deal of evidence for the ionic character of the alkali chlorides, and thus for these systems we should expect the theory to yield excellent results. With the exception of CsCl, these crystals are found in the *B1* structure. Experimentally CsCl is found in the *B2* structure; in this section we report the first electron-gas results for this crystal.¹² First, we consider the experimental structures and then compare these results with those in the alternative *B2* (or *B1*) and *B3* structures. Since all the lattices considered here are cubic, by fixing the ionic positions in the primitive unit cell, the equilibrium geometry and dissociation energy may be determined from energy minimization of a single parameter. The results of these calculations are found in Table I, along with the experimental values. For comparison we also include the results of Cohen and Gordon,^{16(a)} which were obtained using gas-phase Cl^- wave functions in a pairwise additive approximation.

First, let us consider the calculated results in the experimentally determined structures. The overall agreement between the calculated and ex-

perimental lattice constants and dissociation energies is excellent. The average percentage error in the lattice constant $|\bar{a}|$ is 1.3%, and the average percentage error in D_e is 2.1%. None of the results are significantly worse than these average errors. Generally, but not always, the calculated lattice constants are too small, as are the calculated dissociation energies, and there is no systematic variation of these errors with the electronegativity of the metallic component.

The nonlinear many-body effects are relatively small. In LiCl, where the Cl^- ions overlap considerably, the difference between the free-ion two-body and many-body results is -2.6% in $|\bar{a}|$ and $+2.4\%$ in D_e . As was found for lithium and sodium fluoride, the many-body theory for LiCl and NaCl leads to a smaller dissociation energy and larger unit-cell volume than the two-body results for the same wave functions. This is due to a net reduction of the many-body exchange energy from the two-body value.

The calculations with the SS anions for LiCl and NaCl are in better agreement with experiment than the results from the gas-phase anions. The use of the SS wave functions is of less importance in the other alkali chlorides. As the effective size of the cation increases and the unit-cell volume increases, the anion site potential decreases. In KCl and RbCl the many-body SS ion results for $|\bar{a}|$ are in slightly worse agreement with experiment than the two-body, gas-phase wave-function¹⁶ results. The dissociation energies in the two types of calculations are virtually the same, however. In CsCl the SS wave function gives a larger unit-cell volume, which is closer to the experimental value, than the free ion. This differs with all previous results where contraction of the anion led to a denser crystal. Here it appears that the use of the contracted SS Cl^- wave function leads to a reduction in magnitude of the net nonpoint Coulomb $\text{Cl}^- - \text{Cl}^-$ potential, which is attractive at large separations. This leads to an expansion of the lattice and a smaller dissociation energy.

The trends in the relative stability of the *B1*, *B2*, and *B3* phases are in agreement with qualitative ion-radius-ratio arguments. The *B3* phase is most favored for small cations. Thus in LiCl the model incorrectly predicts the *B3* structure to be very slightly (1.6 kcal/mole) more stable than the observed *B1* structure. This is not surprising since a similar error occurred for LiF.⁸ As cation size increases from NaCl to RbCl, the *B3* form becomes progressively less stable relative to the *B1*, while the *B2* structure becomes closer in energy to the *B1*. For NaCl, KCl, and RbCl, the *B1* phase is correctly predicted to have

the largest dissociation energy of the three crystal forms. Another error occurs in CsCl, however, where the *B1* structure is still calculated to be the preferred structure. These errors further substantiate our previous conclusion⁸ that the model underestimates the stability of structures with higher coordination number in favor of those with lower coordination number. This result also occurs in a number of semiempirical theories.^{3,4}

An obvious source of this type of error in the electron-gas theory is in the neglect of long-range attractive dispersion forces which act to stabilize the more dense phases with higher coordination number. The dispersion energies in ionic crystals may be estimated by the methods described previously.⁸ This type of analysis for LiCl shows that the dispersion energy in the *B1* phase will be about 1.8 kcal/mole greater in magnitude than in the *B3* phase. As is seen from Table I, the addition of this difference to ΔD_e now makes the correct phase (*B1*) most stable for LiCl, by a very small energy difference (about 0.2 kcal/mole). In CsCl the net dispersion energy in the *B2* phase is about 1.7 kcal/mole greater in magnitude than in the *B1* phase. Adding this amount to the energy difference between the two phases in Table I, we see that the *B1* remains slightly more stable (by about 2.6 kcal/mole) than the *B2* phase. The error in the prediction of the relative stability of the different phases of CsCl thus appears to be due to other factors in addition to the neglect of the long-range dispersion forces.

IV. RESULTS FOR SrF₂ AND SrCl₂

In our previous paper, we gave results for the alkaline-earth fluorides, BeF₂, MgF₂, and CaF₂. We have performed SCF calculations on gas-phase Sr²⁺ and have used the resulting wave function for a number of crystal calculations. In Table II, we present our results for SrF₂ and SrCl₂, which are found in the cubic fluorite structure. The other alkaline-earth chlorides, BeCl₂, MgCl₂, and CaCl₂, are found in distorted structures with polarized Cl⁻ ions, and so have not been included in the present calculations, in which we are assuming unpolarized (spherical) Cl⁻ ions.

The calculated lattice constants and dissociation energies for both of these crystals are extremely close to the experimental values and the errors are typical of those for other halide crystals. For CaF₂, we found⁸ the model predicted that the rutile structure would be slightly more stable than the observed fluorite form. For SrF₂ and SrCl₂, however, the theory gives correct predictions, and the fluorite structure is seen from Table II to be preferred over the rutile. This can be explained

by the larger effective-ion radius in Sr²⁺ than in Ca²⁺. These cation-anion radius ratio arguments appear to be quite effective in explaining many of the electron-gas trends. The larger anion size in SrCl₂ makes the rutile structure closer in energy to the fluorite form than in SrF₂.

V. RESULTS FOR BeO, SrO, SiO₂, KAlO₂, CaTiO₃, AND CaSiO₃

In this section we consider results for a number of oxide crystals, the majority of which contain elements with smaller differences in electronegativity than in the crystals considered previously. It has generally been assumed that most of these crystals are fairly covalent in character. Thus they should be effective test cases for probing the limits of an ionic theory.

Beryllium oxide crystallizes in the hexagonal ZnO or *B4* structure, which is closely related to the *B3* structure.¹⁹ These two structures should be very close in energy and many compounds are found in both forms. The *B4* structure is slightly less symmetric than the *B3*, however. The calculated results for BeO, listed in Table III, are very close to the experimental values despite the small electronegativity difference between beryllium and oxygen. The *B3* structure is predicted to be very slightly more stable than the *B4*. This may be an indication that small distortions and polarization effects, neglected in the theory, play a role in determining greater stability of the *B4* form in the actual crystal.

The calculated results for SrO, which is found in the *B1* structure, are also in good agreement with experiment. The lattice parameter is too small by -1.7% and the calculated dissociation energy is in excess of the experimental value by 3.2%.

There are many well known crystalline polymorphs of silica¹⁹ SiO₂ which have very similar heats of formation. We choose to consider SiO₂ in its high cristobalite form because this is a highly symmetric structure in which there should be no dipolar distortions of the oxide ions. The results for this system are comparable to the results for the more typically ionic systems considered thus far. The calculated lattice constant $|\vec{a}|$ is too small by -2.9% and the error in dissociation energy D_e is -2.0%. We note that the partially converged result, with a more diffuse oxide ion, gave a better result for $|\vec{a}|$ and only a slightly larger error in D_e . This suggests that there may be some small symmetric distortions of the oxide electron density toward the bonding regions between the ions in the actual crystal, which would lead to a larger lattice constant and dis-

TABLE I. Equilibrium geometries and dissociation energies for the alkali chlorides. Unless otherwise indicated, all quantities are in atomic units.

Crystal	Structure		$ \vec{a} ^a$	$-W_B^b$	D_e^c	$\Phi_i(\vec{r}_i)^d$	$-N_i/\gamma_0^e$	r_0^f	ΔD_e (kcal/mole) ^g
LiCl	B1	free ion, two body ^h	6.95	0.3219	0.3219		0.0	∞	
	B1	free ion, many body	7.132	0.3114	0.3114	0.347	0.0	∞	
	B1	SS ion, many body	6.829	0.3294	0.3199	0.362	0.357	2.8	
	B1	expt.	6.868 ⁱ		0.3270 ^j				
	B2	free ion, two body ^h	6.11	0.3037	0.3037		0.0	∞	-11.4
	B2	free ion, many body	6.310	0.2905	0.2905	0.324	0.0	∞	-13.1
	B2	SS ion, many body	6.137	0.3011	0.2948	0.332	0.333	3.0	-15.8
	B3	free ion, many body	7.545	0.3135	0.3135	0.355	0.0	∞	1.3
	B3	SS ion, many body	7.244	0.3319	0.3224	0.369	0.357	2.8	1.6
NaCl	B1	free ion, two body ^h	7.83	0.2867	0.2867		0.0	∞	
	B1	free ion, many body	7.927	0.2816	0.2816	0.311	0.0	∞	
	B1	SS ion, many body	7.655	0.2946	0.2891	0.323	0.323	3.1	
	B1	expt.	7.536 ⁱ		0.2991 ^j				
	B2	free ion, two body ^h	6.73	0.2772	0.2772		0.0	∞	-6.0
	B2	free ion, many body	6.851	0.2703	0.2703	0.298	0.0	∞	-7.1
	B2	SS ion, many body	6.650	0.2805	0.2764	0.306	0.303	3.3	-8.0
	B3	free ion, many body	8.619	0.2767	0.2767	0.310	0.0	∞	-3.04
	B3	SS ion, many body	8.375	0.2885	0.2831	0.319	0.3225	3.1	-3.8
KCl	B1	free ion, two body ^h	8.39	0.2711	0.2711		0.0	∞	
	B1	SS ion, many body	8.320	0.2740	0.2710	0.297	0.286	3.5	
	B1	expt.	8.410 ⁱ		0.2727 ^j				
	B2	free ion, two body ^h	7.14	0.2656	0.2656		0.0	∞	-3.4
	B2	SS ion, many body	7.139	0.2656	0.2626	0.285	0.286	3.5	-5.3
	B3	SS ion, many body	9.180	0.2657	0.2627	0.291	0.286	3.5	-4.6
	B1	free ion, two body ^h	8.71	0.2629	0.2629		0.0	∞	
	B1	SS ion, many body	8.632	0.2656	0.2626	0.286	0.286	3.5	
	B1	expt.	8.795 ⁱ		0.2539 ^k				
RbCl	B2	free ion, two body ^h	7.37	0.2593	0.2593		0.0	∞	-2.3
	B2	SS ion, many body	7.361	0.2597	0.2567	0.277	0.286	3.5	-3.7
	B3	SS ion, many body	9.588	0.2564	0.2534	0.279	0.286	3.5	-5.8
	B2	free ion, two body	7.579	0.2581	0.2581		0.0	∞	-1.5
	B2	free ion, many body	7.550	0.2519	0.2519	0.270	0.0	∞	-4.6
	B2	SS ion, many body	7.689	0.2507	0.2489	0.265	0.270	3.7	-4.3
	B2	expt.	7.792 ⁱ		0.2543 ^j				
	B1	free ion, two body	8.935	0.2605	0.2605		0.0	∞	
	B1	free ion, many body	9.180	0.2593	0.2593	0.268	0.0	∞	
CsCl	B1	SS ion, many body	9.021	0.2575	0.2557	0.274	0.270	3.7	
	B3	SS ion, many body	9.970	0.2487	0.2469	0.268	0.270	3.7	-5.5

^a Length of primitive unit-cell axis.^b Binding energy relative to cations and SS anions.^c Dissociation energy relative to cations and gaseous anions.^d Anion-site potential.^e Shell potential.^f Shell radius.^g Difference in dissociation energy between this phase and the comparable result for the B1 phase.^h Reference 16(a).ⁱ Experimental result for 298 K from Ref. 3 quoted in Ref. 16(a).^j Experimental result for 0 K calculated from thermodynamic data in Refs. 17 and 18.^k Experimental value at 298 K from Ref. 3.

sociation energy than calculated by our purely ionic theory.

It is also apparent from Table III that, as we consider crystals with ions of high charge, the dissociation energies become considerably larger than for our previous calculations. Thus the absolute error in D_e can be quite large, when the

percentage error is still small. We postpone further discussion of this point until Sec. X.

The structure of $KAlO_2$ is similar to that of high cristobalite and so we include it in this section. In this crystal the Al^{3+} and O^{2-} ions occupy the positions of Si^{4+} and O^{2-} , respectively, in high cristobalite, and the K^+ ions occupy interstitial posi-

TABLE II. Results for SrF₂ and SrCl₂. Notation is the same as in Table I. All results were obtained with the many-body theory and the SS ions.

Crystal	Structure		$ \bar{a} $	$ \bar{c} $	u	$-W_B$	D_e	$\Phi_i(\bar{r}_i)$	$-N_i/r_0$	r_0
SrF ₂	Fluorite	partially converged	7.762			0.9636	0.9557	0.371	0.392	2.55
	Fluorite	self-consistent	7.777			0.9613	0.9547	0.370	0.377	2.65
	Fluorite	expt.	7.750 ^a				0.9506 ^b			
	Rutile	self-consistent	10.488	7.083	0.308	0.9537	0.9458	0.385	0.392	2.55
SrCl ₂	Fluorite	partially converged	9.185			0.8225	0.8099	0.314	0.333	3.0
	Fluorite	self-consistent	9.223			0.8182	0.8100	0.313	0.303	3.3
	Fluorite	expt.	9.322 ^a				0.8195 ^b			
	Rutile	self-consistent	12.517	8.208	0.305	0.8189	0.8063	0.327	0.333	3.0

^aReference 19.^bCompiled from data in Refs. 17 and 18 for 298 K.

tions in the unit cell.¹⁹ Although thermochemical data for the heat of formation of this crystal is unavailable, the calculated lattice constant is in good agreement with the experimental result.

CaTiO₃ is one of many compounds with the perovskite structure. Although more precise

structure determinations have shown many of these compounds to be slightly distorted to a less symmetric, orthorhombic lattice rather than the ideal cubic perovskite form,¹⁹ we will consider the simpler ideal form only. For our purposes, the differences between the two forms should be negli-

TABLE III. Equilibrium geometries and dissociation energies for BeO, SrO, SiO₂ (high cristobalite), KAlO₂, CaTiO₃, and CaSiO₃ (perovskite). Notation is the same as in Table I.

Crystal	Structure		$ \bar{a} $	$ \bar{c} $	u	$-W_B$	D_e	$\Phi_i(\bar{r}_i)$	$-N_i/r_0$	r_0
BeO	B4	partially converged	5.227	8.145	0.376	1.7885	1.3873	1.04	1.0	2.0
	B4	self-consistent	5.137	8.065	0.376	1.8141	1.3898	1.06	1.05	1.9
	B4	expt.	5.099 ^a	8.277	0.378		1.4048 ^b			
	B3	self-consistent	5.086			1.8168	1.3925	1.05	1.05	1.9
SrO	B1	partially converged	6.644			1.3270	0.9722	0.744	0.877	2.28
	B1	self-consistent	6.777			1.2915	0.9763	0.730	0.756	2.65
	B1	expt.	6.895 ^a				0.9463 ^c			
SiO ₂	High cristobalite	partially converged	9.577			5.1283	4.2798	1.19	1.05	1.90
	High cristobalite	self-consistent	9.288			5.3113	4.3049	1.23	1.21	1.65
	High cristobalite	expt.	9.567 ^a				4.3944 ^c			
KAlO ₂	Cubic	partially converged	10.355			3.6071	2.8049	0.929	1.0	2.0
	Cubic	self-consistent	10.549			3.5216	2.7964	0.912	0.909	2.2
	Cubic	expt.	10.276 ^a							
CaTiO ₃	Perovskite	partially converged	7.192			5.9926	4.7892	0.899	1.0	2.0
	Perovskite	self-consistent	7.311			5.8723	4.7761	0.885	0.909	2.2
	Perovskite	expt.	7.257 ^a				5.0207 ^d			
CaSiO ₃	Perovskite	partially converged ^{e,f}	6.819			6.2834	5.1873	0.951	0.909	2.2
	Perovskite	self-consistent ^{e,f}	6.766			6.3536	5.2086	0.957	0.952	2.1
	Perovskite	self-consistent ^{g,h}	6.684			6.1900	5.0449	0.970	0.952	2.1
	Perovskite	self-consistent ^{g,i}	6.713			6.1587	5.0137	0.966	0.952	2.1
	Perovskite	expt.	6.586 ⁱ							

^aReference 19.^bCompiled from data in Refs. 17 and 18 for 0 K.^cCompiled from data in Refs. 17 and 18 for 298 K.^dCompiled from data in Refs. 18 and 21 for 298 K.^eZero-pressure result.^fCorrection factors for 28 electrons.^gCalculated for $P=160$ kbar, PV term included in $-W_B$ and D_e .^hCorrection factors for 20 electrons.ⁱReference 20 at 160 kbar.

gible. The calculated lattice parameter for this system is seen to be in excellent agreement with the experimental value. The error in D_e is -4.9% and is somewhat larger in magnitude errors than for the crystals considered so far. Because D_e is very large, the absolute error in energy for this system is quite large.

At pressures of ~ 160 kbar, CaSiO_3 has been shown to undergo a structural transformation to a perovskite structure.²⁰ We calculated $|\vec{a}|$ and D_e at pressures of 0 and 160 kbar for this system. An ambiguity in the proper use of the Waldman-Gordon¹⁰ correction factors arises for this system since there are two types of nearest-neighbor interactions, one with a total of 20 electrons and the other with 28 electrons. Our results in Table III, using the two sets of correction factors, are very similar, however. At 160 kbar the average of the two $|\vec{a}|$ values is close to the experimental result. There is no published value of ΔH_f^0 for this crystal, but a lower bound to this quantity can be obtained from ΔH_f^0 for wollastonite, the stable low-pressure form of CaSiO_3 . The calculated D_e value of this mineral is 5.4443 a.u.,¹⁸ which is somewhat larger than our zero-pressure results for the perovskite form. Quantitatively, this means that our calculated D_e value for perovskite CaSiO_3 is no more than 4.3% smaller than the (unknown) experimental value.

VI. RESULTS FOR ALKALI- AND ALKALINE-EARTH SULFIDES

Sulfide crystals can be treated by an ionic theory as containing cations and dinegative anions. Calculations on sulfides by the electron-gas theory are analogous to those for oxides in that S^{2-} is unstable in the gas phase and experimentally unobservable. The incorporation of a spherical-shell potential in the Hartree-Fock calculations approximates the crystalline potential and gives bound S^{2-} wave functions.

Over the years a number of "cohesive" energy calculations for sulfides have been reported.^{6,7} As was the case for oxides,^{5,7} there are many inconsistencies in these calculations. The cohesive energy is defined as the crystal energy relative to infinitely separated cations and S^{2-} ions, and is not a quantity obtainable from experiment. Thermochemical values for the cohesive energy require values for the electron affinity of the S^- ion, which, in this case, is the difference in energy between the S^{2-} ion in the crystal and the free S^{-1} ion. This quantity obviously varies from crystal to crystal and reported values for this electron affinity^{6,7} represent averages for a range of crystals. Furthermore, since these values are

obtained in part from semiempirical lattice energy calculations, they hardly represent experimental quantities.

A far more appropriate quantity, which is obtainable either from completely theoretical or completely experimental methods, is the dissociation energy D_e of the sulfide crystal into cations, free $\text{S}^{1-}({}^2P)$ anions, and free electrons. A clear comparison between experiment and theory can be made for this energy.

The binding energy W_B obtained from the electron-gas calculations is the crystal interaction energy relative to free cations and free SS sulfide anions. To complete the theoretical energy cycle, we must add the difference in energy between the SS $\text{S}^{2-}({}^1S)$ species and the free $\text{S}^{1-}({}^2P)$ ion to W_B . The Hartree-Fock energy of $\text{S}^{1-}({}^2P)$ is $-397,5382$ a.u.,²² and the Hartree-Fock energy expectation values for the SS ions are obtained in the SCF calculations. As was the case for oxide calculations, we should consider correlation and relativistic energy differences as well. Following Clementi *et al.*,²³ we take the correlation and relativistic energy difference between all SS $\text{S}^{2-}({}^1S)$ ions and the free $\text{S}^{1-}({}^2P)$ ion to be the same as the difference between $\text{Ar}({}^1S)$ and $\text{Ar}^+({}^2P)$ or -0.0359 a.u. The net atomic energy differences for the results reported in Table IV may be obtained from the difference between $-W_B$ and D_e .

The alkali sulfides are found experimentally in the CaF_2 structure. Calculations were performed on this structure only, and no alternative forms were investigated. The agreement between theoretical and experimental results for these crystals is close to that obtained for more ionic systems. The average absolute error in geometry is 2.1%, with no systematic variation as we proceed from lithium to rubidium. The greatest errors in $|\vec{a}|$ are for K_2S and Li_2S , the smallest errors are for Na_2S and Rb_2S . Conclusions based on errors in D_e will be somewhat suspect, since experimental uncertainties in the energies of these crystals are higher than in compounds treated previously.¹⁷ The errors in D_e vary in sign as we go from Li_2S to Rb_2S , and as the average absolute error is only 2.3%, there does not appear to be any breakdown of the model.

With the exception of BeS, the alkaline-earth sulfides are found in the B1 structure. Because of the smaller cation-anion radius ratio, the B3 phase is most stable in BeS. For all systems but BeS, the model continues to give good agreement with experiment. The calculated values of $|\vec{a}|$ are all slightly too small, but the average absolute error is only 2.1%. Excluding BeS, the calculated dissociation energies are close to the experimental results. The error in D_e for BeS is -8.4% ,

which is more than twice the error found in most systems considered previously. The calculated lattice constant for BeS differs from the experimental by only -2.7% , however. In proceeding from BeS to SrS, the error in D_e goes from negative to positive which may be indicative of minor covalent effects in MgS, CaS, and SrS with substantially larger covalent contributions in BeS.

In addition to the experimental structures, we calculated the stability of the B1 phase for BeS and the B3 phase for MgS. The theory gives the correct predictions in these cases, but again both structures are very close in energy.

VII. RESULTS FOR ALKALI AND MAGNESIUM HYDRIDES

Hydride crystals have been treated as ionic crystals in a number of Born-Mayer-type calculations.²⁶⁻²⁸ In applying the electron-gas theory to these systems, we employ SS H^- densities which are more contracted than the gas-phase H^- density. In *ab initio* calculations on gas-phase H^- the correlation energy should be considered, since Hartree-Fock theory predicts H^- is not a stable gas-phase species.²⁹ This is not a problem for crystalline H^- because the inclusion of a shell potential in the Hartree-Fock calculations leads to a bound species with total energy intermediate between that of gas-phase H^- and He. To calculate the dissociation energy of the hydride crystals into cations and free H^- anions, we add the difference in energy between gas-phase H^- and the SS H^- to $-W_B$. We assume no correlation energy differences between the two species. The Hartree-Fock energy of the SS species without the shell potential is obtained from the SCF calculations, and we take the Hartree-Fock energy of gas-phase H^- to be -0.48793 a.u.^{30,31}

The calculated dissociation energies and equilibrium geometries for the alkali hydrides in the B1 structure and the rutile form of MgH_2 are listed in Table V. The first set of calculations, using the Waldman-Gordon¹⁰ (WG) correction factors for the energy density functionals, showed progressively larger errors as we proceeded from LiH to CsH. For the heavier metal ions, we obtained lattices that were too dense and excessively large values for D_e . A similar pattern for the pair potentials of the heteronuclear helium rare-gas dimers can be seen in the WG results.¹⁰ In these systems the position of the well minimum becomes progressively too small and the well depth becomes too large in proceeding from HeHe to HeXe. These errors suggest that for helium- and hydride-ion systems the correction factors, rather than the densities, are in error and that they should be modified in

such a way that the helium or hydride ion is weighted more heavily in their determination.

There is a simple way of accomplishing this, which leads to substantially improved results. In the WG formulation the correction factors are determined from both the total number of electrons in the two atoms or ions and the total number of valence electrons. A two-electron system is weighted more heavily if we use twice the geometric mean number of electrons instead of the total number of electrons to determine these factors. Correction factors determined this way are referred to as geometric mean correction factors in Table V.

These correction factors give much better results for KH, RbH, and CsH than the WG factors. The errors for these crystals are then comparable to those for the systems considered previously, although we still obtain a rather large D_e value for CsH. The results for LiH are also in excellent agreement with experiment. Rather large and surprising errors are found for NaH and MgH_2 . The equilibrium lattice parameters for these two crystals are too large by 7.1% for NaH and 5.6% for MgH_2 . The D_e values for NaH and MgH_2 are too small by -3.3% and -3.4% , respectively. These anomalous results suggest that the Na^{1+} and Mg^{2+} densities are too diffuse.

The overall average errors for the hydride crystals (3.0% in geometry and 2.5% in D_e) are essentially no larger than the errors for more ionic crystals. The pattern of the errors indicates no substantial covalent effects. A non-ionic theory for the binding in these crystals has been proposed^{34,35} in which all valence electrons are treated as a "nearly-free-electron gas." Although this model leads to errors in the geometry comparable with ours, it gives completely unreliable values for the dissociation energy.

VIII. EQUILIBRIUM GEOMETRIES AND DISSOCIATION ENERGIES FOR NITRIDE CRYSTALS

Although the N^{3-} ion is not a stable gas-phase species, there is some evidence that nitrogen in some crystals has properties of a triply charged negative ion.³⁶ In view of its low electronegativity, this is surprising, and nitride crystals should prove to be excellent additional test cases for determining the limits of applicability of the present ionic model. Here we report results for a number of nitrides found in highly symmetric structures.

For the application of the electron-gas theory, SCF calculations on SS N^{3-} ions were performed with a shell charge of $+3$ and varying shell radii. Since $N^{-(3P)}$ is unstable with respect to dissocia-

TABLE IV. Results for alkali and alkaline-earth sulfides. Notation is the same as in Table I. All results were obtained from the many-body theory with SS sulfide ions.

Crystal	Structure		$ \vec{a} $	$-W_B$	D_e^a	$\Phi_i(\vec{r}_i)$	$-N_i/r_0$	r_0
Li ₂ S	Fluorite	partially converged	7.112	1.0743	0.7411	0.752	0.851	2.35
	Fluorite	self-consistent	7.385	0.9867	0.7241	0.724	0.714	2.8
	Fluorite	expt.	7.627 ^b		0.7130 ^c			
Na ₂ S	Fluorite	partially converged	8.524	0.8663	0.6037	0.627	0.714	2.8
	Fluorite	partially converged	8.704	0.8451	0.6113	0.615	0.645	3.1
	Fluorite	self-consistent	8.781	0.8367	0.6119	0.609	0.625	3.2
K ₂ S	Fluorite	partially converged	9.385	0.7921	0.5673	0.568	0.625	3.2
	Fluorite	self-consistent	9.526	0.7758	0.5742	0.562	0.556	3.6
	Fluorite	expt.	9.876 ^b		0.5618 ^c			
Rb ₂ S	Fluorite	partially converged	10.000	0.7460	0.5444	0.535	0.556	3.6
	Fluorite	self-consistent	10.094	0.7385	0.5455	0.523	0.526	3.8
	Fluorite	expt.	10.022 ^b		0.5294 ^d			
BeS	B3	partially converged	6.385	1.4637	1.1590	0.839	0.800	2.5
	B3	self-consistent	6.306	1.4850	1.1518	0.850	0.851	2.35
	B3	expt.	6.481 ^b		1.2571 ^e			
BeS	B1	self-consistent	6.029	1.4411	1.1364	0.822	0.800	2.5
MgS	B1	partially converged	6.724	1.3127	1.0088	0.736	0.800	2.5
	B1	self-consistent	6.880	1.2806	1.0180	0.719	0.714	2.8
	B1	expt.	6.953 ^b		1.0488 ^f			
CaS	B3	partially converged	7.176	1.3113	1.0066	0.745	0.800	2.5
	B1	partially converged	7.361	1.2025	0.9399	0.672	0.714	2.8
	B1	self-consistent	7.474	1.1794	0.9456	0.661	0.645	3.1
SrS	B1	expt.	7.604		0.9373			
	B1	partially converged	7.8191	1.1367	0.9029	0.631	0.645	3.1
	B1	self-consistent	7.800	1.1283	0.9035	0.626	0.625	3.2
	B1	expt.	8.044 ^b		0.8879 ^g			

^aDissociation energy in a.u. into cations, S²⁻(²P) anions and free electrons.

^bReference 19.

^cThermodynamic data for 298 K from Ref. 17. ΔH_f^0 for Li₂S from Ref. 24.

^dThermodynamic data for 298 K from Refs. 18 and 25.

^eThermodynamic data for 298 K from Ref. 18.

^fThermodynamic data for 0 K from Refs. 17 and 18.

^gThermodynamic data for 298 K from Refs. 17 and 18.

tion into neutral N(⁴S) and an electron, the appropriate dissociation energy for comparison of theory and experiment in these systems is the energy relative to cations, free atomic nitrogen, and free electrons. Energy differences between SS N³⁻(¹S) and N(⁴S) were calculated using -54,400.92 a.u. for the Hartree-Fock energy²² of N(⁴S) and -0.188 a.u. for its correlation energy.³⁷ In addition, the correlation energy for all the SS N³⁻ anions has been assumed equal^{16 (b), 37} to that of O²⁻(¹S) or -0.406 a.u.

A. Results for BN, AlN, and ScN

The preferred form for boron nitride is the B3 structure, while for AlN it is the B4 structure. The cation-anion radius ratio is larger in ScN, and it is found to have the B1 structure. We list our results for these crystals in Table VI.

While the calculated lattice parameters are all

in good agreement with experiment, there are some larger errors in the calculated values of D_e . For BN the percentage error in D_e of -7.9% is a rather large deviation from experiment. In AlN, as for BeO, the B4 structure is almost identical in energy with the B3 form. Again the more symmetric B3 form is predicted to be slightly more stable than the B4. The calculated D_e value, in either lattice, is very close to experiment, however. For ScN the calculated value of D_e is too large by 3.7%.

B. Results for Be₃N₂ and Li₃N

Both beryllium nitride and lithium nitride are found in hexagonal lattices.^{19, 38, 39} Since there are ten ions per unit cell in Be₃N₂, the number of points in the three-dimensional quadratures for this system was increased⁴⁰ to 3722. We varied the lengths of the \vec{a} and \vec{c} axes in minimizing W_B

TABLE V. Results for alkali hydrides and magnesium hydride. Notation is the same as in Table I. All results were obtained with the many-body theory and $SS\ H^{-1}$ anions

Crystal	Structure		$ \vec{a} $	$ \vec{c} $	u	$-W_B$	D_e^a	$\Phi_i(\vec{r}_i)$	$-N_i/r_0$	r_0
LiH	B1	partially converged	5.495			0.3845	0.3506	0.452	0.476	2.1
	B1	self-consistent	5.564			0.3782	0.3500	0.447	0.444	2.25
	B1	expt.	5.459 ^b				0.3459 ^c			
NaH	B1 ^d	partially converged	6.659			0.3254	0.2971	0.371	0.444	2.25
	B1 ^d	self-consistent	6.978			0.3097	0.2951	0.355	0.357	2.8
	B1 ^e	self-consistent	6.987			0.3091	0.2945	0.353	0.357	2.8
KH	B1	expt.	6.521 ^b				0.3044 ^c			
	B1 ^d	partially converged	7.635			0.2851	0.2705	0.324	0.357	2.8
	B1 ^d	self-consistent	7.515			0.2887	0.2785	0.329	0.323	3.1
RbH	B1 ^f	self-consistent	7.699			0.2817	0.2716	0.321	0.323	3.1
	B1	expt.	7.617 ^b				0.2708 ^c			
	B1 ^d	self-consistent	7.727			0.2842	0.2741	0.320	0.323	3.1
CsH	B1 ^h	partially converged	8.042			0.2726	0.2624	0.307	0.323	3.1
	B1 ^h	self-consistent	8.073			0.2714	0.2633	0.306	0.303	3.3
	B1	expt.	8.067 ^b				0.2574 ⁱ			
MgH ₂	B1 ^d	self-consistent	7.840			0.2836	0.2734	0.316	0.323	3.1
	B1 ^j	partially converged	8.401			0.2657	0.2555	0.294	0.323	3.1
	B1 ^j	self-consistent	8.377			0.2662	0.2591	0.293	0.295	3.4
MgH ₂	B1	expt.	8.520 ^b				0.2482 ^k			
	rutile ^d	partially converged	8.746	6.072	0.311	1.0657	0.9978	0.456	0.476	2.1
	rutile ^d	self-consistent	8.866	6.142	0.312	1.0497	0.9932	0.453	0.444	2.25
	rutile ^e	self-consistent	8.902	6.151	0.312	1.0463	0.9897	0.452	0.444	2.25
	rutile	expt.	8.536 ^l	5.709 ^l	0.306 ^l		1.0244 ^c			

^aDissociation energy of crystal into free cations and $H^{-1}(S)$ anions.

^bReference 19.

^cCompiled from data in Ref. 17 for 0 K.

^dCalculated with Waldman-Gordon (Ref. 10) correction factors.

^eGeometric mean correction factors for NaH and MgH₂: $C_K=1.090$, $C_X=0.719$, and $C_C=0.380$.

^fGeometric mean correction factors for KH: $C_K=1.085$, $C_X=0.793$, and $C_C=0.450$.

^gCalculated from data in Ref. 17 for 298 K.

^hGeometric mean correction factors for RbH: $C_K=1.079$, $C_X=0.873$, and $C_C=0.500$.

ⁱCalculated from data in Refs. 3, 17, and 32 for 298 K.

^jGeometric mean correction factors for CsH: $C_K=1.074$, $C_X=0.913$, and $C_C=0.515$.

^kCalculated from data in Refs. 17 and 32 for 298 K.

^lReference 33.

for these systems and for Be_3N_2 the parameter u ,¹⁹ which determines the equilibrium positions of four of the Be^{2+} ions, was varied as well. The calculated cell volumes for Be_3N_2 and Li_3N are somewhat too small; the average error for $|\vec{a}|$ and $|\vec{c}|$ is -4.4% for both systems. The calculated $|\vec{c}|/|\vec{a}|$ ratio for Li_3N is close to experiment, while that for Be_3N_2 is too large by 6.8% . The D_e value for Be_3N_2 is very close to the experimental value, but for Li_3N the calculated D_e is too large by 6.7% . This discrepancy may be due to our neglect of the zero-point energy in Li_3N . Experimental evidence³⁶ suggests that the force constants for the Li-N interactions in this crystal are considerably larger than in the lithium halide crystals.

The overall pattern of the errors for the nitride crystals may be indicative of some covalent effects. The calculated lattice parameters are, in all but one case, too small, which suggests that

there are contributions to the binding from symmetric distortions of the electronic density away from the anion towards the cation neighbors.

The errors in D_e vary in sign, and go from positive to negative as the electronegativity of the metallic species increases. As for some oxide crystals, the dissociation energies in these crystals are fairly large. This means that the errors in absolute energy will be considerably larger than, for example, the alkali-halide crystals, even when the percentage error in D_e is quite reasonable.

IX. RESULTS FOR AlP, Be_2C , AND SiC

Our results thus far have shown that the ionic electron-gas theory works quite well for most of the systems treated. There are a few isolated examples where errors in either the calculated

TABLE VI. Equilibrium geometries and dissociation energies for nitride crystals. Notation is the same as in Table I. These results were obtained with SS N^{3-} anions and the many-body theory

Crystal	Structure		$ \vec{a} $	$ \vec{c} $	u	$-W_B$	D_e^a	$\Phi_i(\vec{r}_i)$	$-N_i/r_0$	r_0
BN	B3	partially converged	4.801			4.2193	2.8676	1.68	1.58	1.9
	B3	self-consistent	4.682			4.3466	2.8673	1.72	1.71	1.75
	B3	expt.	4.831 ^b				3.1115 ^c			
AlN	B4	partially converged	6.133	9.418	0.394	3.3767	2.3372	1.34	1.2	2.5
	B4	self-consistent	5.867	9.146	0.385	3.5361	2.3709	1.39	1.36	2.2
	B4	expt.	5.879 ^b	9.407	0.385		2.3793 ^c			
	B3	self-consistent	5.795			3.5400	2.3748	1.39	1.36	2.2
ScN	B1	partially converged	5.842			3.2913	2.1260	1.27	1.36	2.2
	B1	self-consistent	5.978			3.2055	2.1279	1.24	1.25	2.4
	B1	expt.	5.933 ^b				2.052 ^d			
Be ₃ N ₂	hexagonal	partially converged	4.936	17.455	0.079	6.9374	3.9788	1.58	1.71	1.75
	hexagonal	self-consistent	5.025	18.394	0.078	6.7413	4.0379	1.54	1.58	1.9
	hexagonal	expt.	5.369	18.317	0.075		3.9788 ^c			
Li ₃ N	hexagonal	self-consistent	6.643	6.903		2.1238	1.0834	1.20	1.20	2.5
		expt.	6.894 ^e	7.323			1.0156 ^c			

^aDissociation energy to cations, gaseous, neutral nitrogen atoms, and free electrons.

^bReference 19.

^cCompiled from data in Refs. 17 and 18 for 0 K.

^dCompiled from data in Refs. 18 and 25 for 298 K.

^eStructural data from Ref. 38.

lattice parameters or dissociation energies are markedly larger than for most of the other cases. As a whole, the nitride crystal results show somewhat larger errors in both quantities than the other results. In order to test the theory further, we have chosen AlP, Be₂C, and SiC as extreme limits for an ionic theory.

For the phosphide calculation, we used SS $P^{3-}(^1S)$ wave functions. The calculation of the dissociation energy in this case refers to infinitely separated Al³⁺ cations, P(⁴S) atoms, and electrons. The Hartree-Fock energy²² of P(⁴S) was taken to be -340.7186 a.u. In order to estimate the correlation and relativistic energy differences between SS $P^{3-}(^1S)$ and P(⁴S), we used the methods and values suggested by Clementi *et al.*²³ The net three-electron ionization in going from $P^{3-}(^1S)$ to P(⁴S) was separated into three single-electron

steps. The change in correlation and relativistic energy for each of these steps was then assumed to be the same as for the ionization of the isoelectronic neutral species. The net correlation and relativistic energy difference between $P^{3-}(^1S)$ and P(⁴S) is then found to be -0.1291 a.u.

Be₂C and SiC were treated as consisting of cations and C⁴⁻ units. The dissociation energy refers to Be²⁺ or Si⁴⁺ ions, electrons, and C(³P) at infinite separation. The Hartree-Fock energy²² of C(³P) is -37.6886 a.u. and its correlation energy³⁷ is -0.158 a.u. For C^{4-}(^1S), we took the correlation energy to be the same as for the isoelectronic O^{2-}(^1S) species³⁷ or -0.406 a.u. This is probably only a rough estimate of the actual value, but errors introduced this way will only effect D_e and not the equilibrium geometry.}}

As might be anticipated, the results for these

TABLE VII. Results for AlP, Be₂C and SiC.

Crystal	Structure		$ \vec{a} $	$-W_B$	D_e	$\Phi_i(\vec{r}_i)$	$-N_i/r_0$	r_0
AlP	B3	self-consistent	6.785	3.0708	2.1146	1.18	1.2	2.5
	B3	expt.	7.284 ^a		2.2720 ^b			
Be ₂ C	Antifluorite	self-consistent	5.428 ^a	5.127	2.5910	1.98	2.0	2.0
		expt.	5.790		2.598 ^b			
SiC	B3	self-consistent	5.368	6.7090	4.1726	2.0	2.0	2.0
	B3	expt.	5.810 ^a		4.2587 ^c			

^aReference 19.

^bCompiled from data in Ref. 18 for 298 K.

^cCompiled from data in Refs. 17 and 18 for 0 K.

three systems in Table VII are substantially poorer than for most other systems. For these crystals, the calculated lattice constants are significantly smaller than the observed values. These errors are all larger, but similar to those in BN, Li_3N , and Be_3N_2 . The average error in a_0 is -6.8% . Errors in D_e are less systematic. For SiC, D_e is too small by 6.9% , but for AlP and Be_2C the calculated D_e values are reasonably close to experiment. It appears that in many cases the ionic model can give as much binding in the crystal as a covalent model by forcing the nuclei slightly closer together than in the actual crystal. A covalent model would give similar binding by charge transfer towards the bonding region between atoms.

X. SUMMARY OF RESULTS

Errors in the electron-gas calculations arise from many different sources. Among these are the approximate form of the density functionals, the additive density approximation, the evaluation of component ionic densities, and the neglect of long-range dispersion forces and zero-point energy. The overall accuracy of the theory depends in part on a cancellation of these individual errors and the net error can be expected to be fairly random from system to system. That this is true even for highly ionic systems is revealed in Figs. 1 and 2, where the percentage errors in the equilibrium geometries and dissociation energies versus absolute electronegativity differences⁹ of the component species have been plotted. We include calculations presented here and in Ref. 8. For the strongly ionic crystals ($|\Delta\chi| \approx 3.0$), our choice of ionic densities is probably fairly accurate, and the major source of error is likely to be in the density functionals. This type of small random error will also be present in calculations on more covalent crystals and will tend to conceal any errors due to breakdown of the ionic model.

There is no simple or obvious correlation of the errors with electronegativity difference to be discerned from these figures. The use of alternative scales of electronegativity^{2,41} leads to very little change in the figures. Over a wide range of electronegativity differences, these errors are quite small. With a few exceptions, the absolute values of the errors in the lattice parameters average to less than 2%, and are almost always within 4.0% for $|\Delta\chi| > 1.0$. This is clearly an acceptable error for many applications and a great number of compounds will fall into this category. Errors in geometry for NaH and MgH_2 are considerably larger than this, however. From Fig. 1 it is apparent that for the other sodium and magnesium crystals, the calculated lattice parameters were

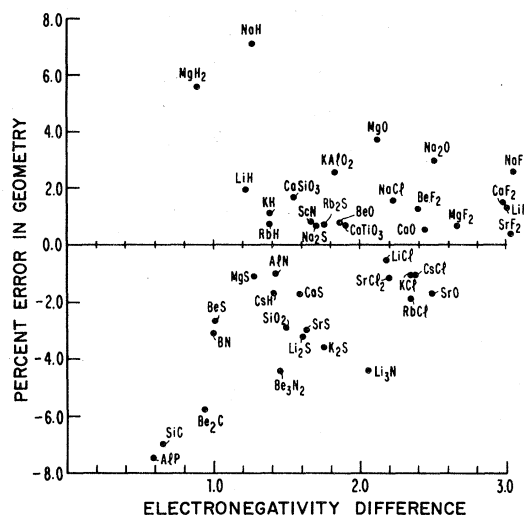


FIG. 1. Percentage errors in calculated equilibrium geometry versus electronegativity difference (Ref. 9).

also too large but with smaller errors. This suggests that the Hartree-Fock Na^{1+} and Mg^{2+} densities are too diffuse. This could be due to the neglect of correlation in the determination of the cation wave functions, which should be a particularly important effect in the second-row cations. Densities from correlated wave functions should be more contracted than the Hartree-Fock densities. For AlP, Be_2C , and SiC, the errors in the lattice parameters are much greater than for the other crystals and show the inadequacy of the ionic model for these systems with $|\Delta\chi| < 1$.

Percentage errors in D_e show much the same sort of scatter as those in the equilibrium geometry. In general for $|\Delta\chi| > 1.0$, D_e is calculated

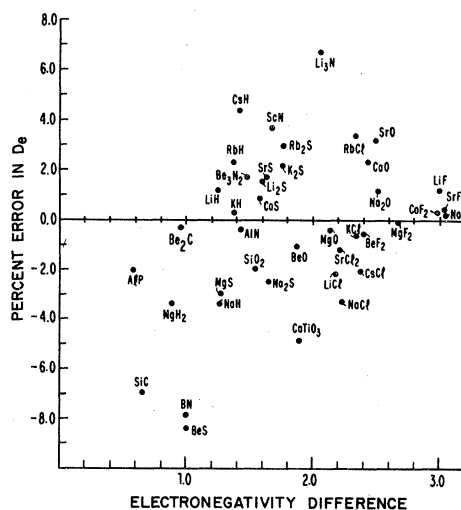


FIG. 2. Percentage errors in dissociation energy versus electronegativity difference (Ref. 9).

to an average absolute error of less than 2%, and usually to within $\pm 4.0\%$. For $|\Delta\chi| \leq 1.0$, D_e is always too small, but, as the results for AlP and Be_2C show, can be fortuitously close to the experimental value.

The bulk of the calculations support the validity of the ionic model for those systems with $|\Delta\chi| > 1.0$. The average absolute error in both the equilibrium geometry and in D_e is only 1.9% in this case. For $|\Delta\chi| \leq 1.0$, the error in at least one of these quantities is significantly greater than these averages. Excluding MgH_2 , the trend in these systems is for the lattice constants to be much too small (average error = - 5.2%) and for D_e to be also too small with an average error of - 5.1%. For $|\Delta\chi| \leq 1$, then, the ionic model is inadequate. As was mentioned in Secs. V and VIII, the absolute errors in D_e can be fairly large for systems with highly charged ions. This is probably an electrostatic effect, since for these systems the electrostatic potentials and fields are larger than in the other crystals, and a given error in the density will lead to a large error in the absolute energy. Thus it is probably best to judge the applica-

bility of the model by the percentage rather than absolute error in D_e .

In many cases, however, a certain degree of accuracy in D_e will be required. Since the percentage error in D_e averages to less than 2%, and is generally less than 4.0% for $|\Delta\chi| > 1.0$, the likely absolute error in D_e for a given system can be easily estimated. The net crystal dissociation energy can be estimated from both W_B and average energy differences between SS anions and the appropriate gas-phase species. W_B is usually close to the Madelung energy of the crystal. A rough estimate of D_e can then be easily found and used to determine the probable error in the electron-gas result. The suitability of the electron-gas theory for a given problem can then be judged.

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their calculation with double precision programming (Ref. 15), we obtained a total energy of only -7553.6918 a.u. By carefully reoptimizing the orbital exponents in Ref. 13, we obtained an analytic wave function with a total energy of -7553.7884 a.u. This is, as expected, slightly greater than the numerical value.

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