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Possible role of charged defects in molecular solids

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The atomistic fundamentals of the initiation of chemical reactions, combustion, or detonation in a molecular solid system is a largely unexplored area. What is clear is that in many molecular solids, largely van der Waals bonded, the solids largely decompose in a way that destroys the integrity of the well-bound molecules rather than dissociating into the constituent molecules. In this paper we explore one possible mechanism for such behavior. We postulate the existence of charged defects in such a system and explore their effects. Because of the presence of charges, molecules polarize. This modifies their interactions with each other and may simultaneously destabilize the constituent molecule.

I. INTRODUCTION

A widely held belief among workers in the energetic-materials community is that initiation (of combustion or detonation) when it occurs in the solid phase is associated with small regions of the energetic system called "hot spots."[1] The evidence for the existence of such hot spots is compelling, but the detailed atomistic description of what constitutes a hot spot and fundamental principles governing its actions are unavailable. This is not to say that substantial amounts of circumstantial evidence are unavailable. We begin by reviewing some of this evidence. It is also true that some energetic solid systems are believed to react in the gas phase. That is, some material is evolved from the solid into the gas prior to initiation. We do not consider such systems in this paper.

In the laboratory, initiation may be accomplished by impacting a pellet of energetic material on or by a hard flyer plate. In such experiments, it is noted that the collision energy is significantly less than the energy needed to thermally initiate the reaction; nonetheless, initiation may reliably result.[2] This has led to the idea that the impact energy concentrates in small regions of the system in sufficient quantity to raise local temperatures to exceed those needed for initiations, hence the designation of such regions as "hot spots." Other ways of initiation include hot wires or other direct application of heat, other forms of shock, or application of static pressure.

Considerable data have been obtained using static loading methods by Swanson and co-workers at Los Alamos National Laboratory, and we will summarize the results in Nitrous oxide (solid N_2O_2).[3] Nitrous oxide is confined in a Merril-Basset cell, and is pressurized slowly. Eventually a critical pressure is reached and a chemical decomposition of the system is observed. In such an experiment vaporization of the solid is highly unlikely to occur before initiation. The possible results of nitrous oxide decomposition are too complex to repeat here and we give only a schematic. If the nitrous oxide is an essentially pure, perfect single crystal, then the reaction products include significant portions of N_2 and O_2. This indicates that decomposition may follow an unimolecular pathway. If the system is polycrystalline and contains significant defects, the reaction proceeds at lower pressure and the reaction products do not include N_2 and O_2, but rather N_2O_2, N_2O_3, and so forth. These products imply that the decomposition pathway is a concerted molecular reaction, involving at least two or three N_2O_2 units. Clearly the presence of both defects and the microstructure is a significant factor in the solid-state chemistry of nitrous oxide. These results indicate that several questions need be answered. One needs to ask why the action of two or three weakly interactive N_2O_2 units are able to cause decomposition of the strongly bonded NO unit.

Further insight is provided by the experiments of T. Dickinson into fracture and fractoemission of energetic and other solids.[4] This data indicates that when such systems fracture (even microcrack formation), a charge separation occurs on the (micro)crack surface. Thus one side is charged positively, the other negatively. This experimental fact seems to hold for ionic systems (e.g. LiF) or for a molecular solid system (e.g., a Wint-o-green lifesaver used in the experiment of Ref. 4). In the case of the molecular solids studied, the system typically lacked a center of inversion symmetry and exhibited piezoelectric characteristics.

Such studies are in reasonable accord with the theoretical ideas promoted by Coffey.[5] Coffey argues that hot spots in crystal are associated with regions of high shear stress. Normally such regions occur at the surface of the sample, but they can be generated internally as well. Such regions are often accompanied by a high density of dislocations and the formation of shear bands. Coffey is less specific in defining the precise physical effect of such regions of the solid on their constituent molecules.

It is not known how the surfaces obtain their charge in general; however, models do exist which account for the charging of the alkali-metal–halide system.[6] It is generally believed that cracking begins when a high density of dislocation is swept to a surface, forming an initial microcrack. This may grow into an actual fracture. In the case of ionic solids the dislocation edge is known to be charged.[7] This is due to both dislocation geometry and the ionic nature of the host. The sweeping of the dislocation to the surface provides a basic mechanism for the charging of a surface. This also allows internal regions to acquire significant charge.

In addition, there may be strong interactions between other charged defects and dislocations. It is also suggested that, via their interaction, other charged defects may be swept to the surface.[4]

None of this explains the charges of nonionic systems. It is worth remembering that many interesting energetic systems are ionic in nature. This includes such common pseudo-alkali-halides as the azides or ammonium perchlorate. Nevertheless, for the piezoelectric nonionic molecular solids, surface charging upon cracking is a fact of life. Possibly the charging is related to the piezoelectric nature of the solid, or perhaps it is due to thermodynamic populations of charged defects in the system,[8] or even a combination of these. This is an area which is unexplored and deserves serious attention in the very near future.

We begin the study reported here by accepting the presence of charges inside an energetic crystal. We do not know where they are, how many there are, how the solid gets them, or what their geometry is. The qualitative results are not very sensitive to these questions. That is, consider the effect of a unit point charge in a unit cell, or a line of charge of infinite length which contains a unit charge per unit cell, or a sheet of charge containing a unit charge per unit cell on a molecule one lattice separation away. The electric field is trivially determined by Gauss's law. Doing this, one finds for these three cases that the field strength ratios are 1:2:2π, respectively. Thus the forces are of the same order of magnitude for all cases.

In this paper we explore the effect of charged defects on the stability of molecular solids. This study is of two types. We consider the effect of the induced polarizations on the intermolecular interactions. This is, in effect, an adaptation of the ideas first given by Mott and Littleton for ionic crystals.[9] We also consider the effect of the charge on the bond strengths of the constituent molecule, that is, on the intramolecular interaction. Similar studies to this for gas-phase energetic molecules in the presence of free radicals are being considered by Ho *et al.*,[10] with qualitatively similar conclusions.

These studies are carried out using cluster modeling for the energetic solid.[11] The first-order studies are performed using the unrestricted Hartree-Fock model (UHF). Correlation corrections are incorporated in all studies by a direct use of many-body perturbation theory (MBPT). Beck and Kunz have shown the utility of this for methane in both ground and excited states.[12] The methods are briefly described in Sec. II. Some simple results are provided in Sec. III. In Sec. IV we draw our conclusions.

II. THEORETICAL METHODS

In this study, we adopt the usual nonrelativistic approach (atomic number ≤ 10 here) and make the Born-Oppenheimer approximation. The system Hamiltonian is given in atomic units ($e=\hbar=m=1$, the energy is in hartrees, 1 hartree ≈ 27.2 eV) as

$$H=-\tfrac{1}{2}\sum_{i=1}^{n}\nabla_i^2-\sum_{i=1}^{n}\sum_{I=1}^{N}\frac{Z_I}{|\mathbf{r}_i-\mathbf{R}_I|}+\tfrac{1}{2}\sum_{i,j=1}^{n}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}+\tfrac{1}{2}\sum_{I,J=1}^{N}{}'\frac{Z_IZ_J}{|\mathbf{R}_I-\mathbf{R}_J|}\;. \tag{1}$$

There are n electrons in the system. The coordinate of the ith electron is $\mathbf{r}_i$. There are N nuclei in the system. The Ith nucleus has atomic number Z_I and coordinate $\mathbf{R}_I$. In this study no core-replacing pseudopotentials are used and therefore no pseudopotential term is needed in our Hamiltonian. We begin by choosing a trial wave function for H in the UHF manner. That is, $\psi(\mathbf{r}_1\rightarrow\mathbf{r}_n)$ is approximated by a single Slater determinant of one-electron orbitals $\phi_i(\mathbf{x}_i)$ where $\phi_i(\mathbf{x}_i)=\phi_i(\mathbf{r}_i)\alpha$ or $\phi_i(\mathbf{r}_i)\beta$. That is, the one-electron orbital is an eigenstate of the z component of the spin angular momentum. The one-electron orbitals are chosen to be orthonormal but are not otherwise constrained. If the orbitals are chosen variationally, they are determined by the usual UHF equation

$$-\tfrac{1}{2}\nabla^2\phi_i(\mathbf{r})-\sum_{I=1}^{N}\frac{Z_I}{|\mathbf{r}-\mathbf{R}_I|}\phi_i(\mathbf{r})+\int\left[\frac{\rho(\mathbf{x}',\mathbf{x}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{x}'-\rho(\mathbf{x},\mathbf{x}')/|\mathbf{r}-\mathbf{r}'|\hat{P}(\mathbf{r}',\mathbf{r})\right]\phi_i(\mathbf{r})=\varepsilon_i\phi_i(\mathbf{r})\;. \tag{2}$$

Here $\hat{P}$ is the operator which interchanges coordinates $\mathbf{r}$ and $\mathbf{r}'$. The first-order density matrix ρ is given as

$$\rho(\mathbf{x},\mathbf{x}')=\sum_{i=1}^{n}\phi_i(\mathbf{x})\phi_i^{\dagger}(\mathbf{x}')\;. \tag{3}$$

Coordinate $\mathbf{x}$ is used to designate both the spatial coordinates and the spin coordinate. We solve this equation by expanding ϕ in a series of contracted Gaussian orbitals. Our recent practice for accomplishing this is given both by Beck and Kunz[12] and by Goalwin and Kunz.[13]

It is well known that the UHF method has the advantage of permitting proper dissociation of chemical bonds,[11] but it definitely neglects electron correlation. In this study, which is aimed at correlation in the solid, methods need to be size consistent.[14] Of the available size-consistent methods, we chose to use the MBPT method. We previously used this method for solid-state calculation of excitation energies in energy-band theory.[15] More recently, Bartlett and co-workers have systematically extended and studied these methods for use on large molecules.[16]

The Hamiltonian is partitioned into two parts, a zeroth-order Hamiltonian H_0, whose eigensolution ϕ_i and eigenvalue W_i are known, and a perturbation V. That is,

$$H \equiv H_0 + V \ . \tag{4}$$

In our case we pick H_0 to be the sum of the one-electron Fock operators in the n spaces. Ultimately this yields an expression for the system energy to second order in V, which is[13]

$$E_i = W_i + V_{ii} + \sum_{j\ (\neq i)} \frac{V_{ji} V_{ij}}{W_i - W_j} \ . \tag{5}$$

Here

$$V_{ij} = \langle \phi_i \mid V \mid \phi_j \rangle \ . \tag{6}$$

Furthermore, if one wishes to approximate all orders higher than the second in V by the dominant terms, order by order, using the result that, in general,

$$O(V_{II}) \approx O(V_{JJ}) >> V_{IJ} \ ,$$

one finds

$$E_i = W_i + V_{ii} + \sum_{j(\neq i)} \frac{V_{ji} V_{ij}}{W_i - W_j} \times [1 - (V_{jj} - V_{jj})/(W_i - W_j)]^{-1} \ . \tag{7}$$

Bartlett has shown that the use of Eq. (5) normally obtains about 90% of the correlation energy contained in a basis set.[16] In the case of molecular methane, Beck and Kunz[12] were able to use this MBPT method to account for 90% of the experimental value of the correlation energy for the ground state. They were also able to compute the energy of the low-lying excited states of methane to similar high accuracy. In the use of Eqs. (5) and (7) one hopes the inclusion of the large contribution to all higher-order terms in perturbation theory will have made a small change in the second-order contribution. If this hope is realized, one may be assured that the perturbation result is well converged. If this is not true, one needs either a better zero-order Hamiltonian, a better basis set, or explicit computation of higher terms in V other than the second.

III. SIMPLE RESULTS

The presence of charged surface patches as seen in the fractoemission studies and also the possible association of charging with point defects and dislocation has prompted us to study the possible role of charged defects in molecular solids. The first study, inspired by the work of Mott and Littleton,[9] raised the question of whether the presence of charged defects could substantially alter the interaction between two molecules in a molecular solid. The assumption here is that the charge causes a molecule to polarize. The dipole moments which are statically induced here will then interact with one another and also with the charge inducing them. These additional electrostatic interactions should modify the apparent intermolecular forces. This interaction is distinct from a van der Waals mechanism in that the interaction here is not due to fluctuating dipoles but rather due to static induced dipoles as well as monopole-dipole interactions.

In order to obtain a quantitative assessment of this mechanism we consider a simple prototype of a molecular system. We consider the interaction of two Ne atoms. Ne is chosen for two reasons: First, the molecule, a Ne atom, has no internal molecular dissociation possible. Therefore our study will not be confused by the presence of intramolecular degrees of freedom. Secondly, the Ne atom is relatively unpolarizable. Thus the effect we wish to study is likely to be a lower bound to the type of effect found in the real-world case. In units of 10^{24} cm^3 for example, the polarizability of Ne is 0.39, whereas Xe is 4.10, F^- is 1.04, K^+ is 0.83, and I^- is 7.10.[17] Nevertheless, as we shall see, the effect of a point charge of size $4e^-$ a lattice constant away from the Ne atom is substantial. The choice of a charge of $4e^-$ was made following our study of charge geometry effects discussed in the Introduction. This charge is intermediate in effect to a line of charge and a sheet of charge and, given the results of Dickenson, seemed a plausible choice.

In this study a rather elaborate Ne basis set was developed. Using this set a polarizability of 0.29×10^{-24} cm^{-3} was obtained for the Ne atom. This is 70% of the experimental result. In the case of two Ne atoms without any free charge, this basis set predicts a well depth for the Ne_2 binding curve of 0.000 072 a.u. This is contrasted with an experimental value of 0.000 138 a.u (Ref. 18). This value is in good agreement with what one expects based upon the polarizability results. It is well known that the van der Waals attraction scales as the polarizability squared. This calculation was repeated in the presence of the point charge. In the first case a linear array of charge —Ne—Ne is used. The Ne farthest from the charge is then removed. In this case the theoretical well depth increases to 0.001 06 a.u., a substantial increase. In the second study the charge is placed equidistant from each Ne. This is a geometry similar to the crystal. In this case one Ne is removed to infinity and the well depth is seen to increase to 0.0141 a.u., a substantial increase. This demonstrates that the presence of free charge in a van der Waals bonded molecular system can dramatically increase the effective intermolecular interaction.

The presence of a negative point charge induces the electron on a given Ne to be repelled from the point charge and the nucleus to be attracted. This polarization of the Ne atom causes its total energy to decrease (i.e., become more negative). Thus, up to a point, the nearer the Ne to a point charge, the more negative the system energy becomes. This tends to attract the Ne to the negative charge. In the case where the neon atoms and the charge form an equilateral triangle initially, the dominant cause for the apparent increase in Ne-Ne attraction is the change in energy of the Ne being removed from point charge. In fact, in this geometry the dipole-dipole interaction is weakly repulsive of itself. In the linear charge —Ne—Ne case the charge again attracts the Ne's, but here the dipole-dipole interaction is also attractive, although weaker than the dipole-monopole interaction. Thus the dominant character in increasing the apparent molecular interaction strength is the dipole-monopole interaction. These size relationships should be a strong function of the size of the polarizability. These interactions being mostly due to polarization effects, the effect of several charges should be the vector sum of the polarizations.

This simple study was repeated for the case of CH_4 (methane). The methane dimer in the absence of a point charge ($4e^-$) was found to be bound by 0.000 034 a.u. In the linear case of charge $—CH_4—CH_4$ the effective bonding is found to increase to 0.0013 a.u., and in the triangular geometry the effective binding increased to 0.0236 a.u. This is similar to the Ne case. In all cases our results include MBPT, otherwise in the absence of a point charge neither dimer would be bound. The UHF level omits van der Waals effects. All calculations are counterpoised to eliminate basis set overlap effects on the binding energies. For calculations in the presence of a point charge, the initial geometry is that for the crystalline case. Finally, in the case of CH_4, intramolecular distortions are neglected.

The second type of study examines the effect of the point charge ($4e^-$) on the internal structure of a molecule. In this case a CH_4 molecule was chosen as our prototype. This is due in part to the high symmetry of CH_4. First, we note in the presence of a charge the total energy of our CH_4 unit increased by 0.0219 a.u. in the UHF case and by 0.0220 a.u. in the MBPT case compared to the CH_4 with no free charge around. The charge was placed at a separation of a first nearest neighbor for solid methane. This bonding increase is in accord with our Ne study and with our intuition from electrostatics.

Considering the CH_4 without a point charge, intitially an H atom was removed. The atom was removed as a neutral entity. The energy to remove the atom was found to be 0.177 a.u. This type of calculation was repeated in the presence of a point charge. For simplicity the geometry of the resulting CH_3 fragment was held to its CH_4 geometry.

In the case of CH_4, the hydrogens are slightly positively charged and the C is somewhat negative. The charge on the C is almost one electron charge. The presence of a negative charge outside the CH_4 serves to drive further electron charge from the hydrogen atom nearest the charge onto the hydrogen atom farthest from the charge. This in turn strengthens the bond of the near hydrogen and weakens the bond of the farthest one. In the present case, constraining the system to dissociate into $H+CH_3$, as neutral entities, the increase in near-bond strength is 0.010 a.u., and the decrease in far-bond strength is 0.0044 a.u. These are not negligible amounts. In this case the H atom is removed to infinite separation from the CH_3.

Much more interesting phenomena occur when the CH_4 decomposition is unconstrained to be into neutral fragments. In this case the details of the path chosen are significant. We chose the following geometry for our study. Consider a cube, the center of whose sides are pierced by the Cartesian axes. A carbon atom is at the cube center and the four hydrogens are tetrahedrally arranged at the cube corners. The extra charge ($4e^-$) is placed a CH_4 nearest-neighbor distance away on the $+z$ axis. Initially one of the hydrogens on the $+z$ side of the cube is moved. We try two trajectories, one in which x and z are constant and y varies, the second for constant x and y, allowing z to increase. That is, in the second trajectory, the H atom initially approaches the excess charge.

The first trajectory produces results in accord with our study where dissociation was constrained to be into neutral fragments. Here the removal energy is found to be 0.187 a.u., an increase of 0.010 a.u. from the case where no charge is present. Similar results are obtained by removing this entity in the $-z$ direction or by removing one of the hydrogens on the $-z$ side of the cube, using the first trajectory. In the case of the second trajectory a much more dramatic event occurs. As the H is initially removed the system energy increases, and the H is atomic H electrically. This continues until the z coordinate has increased by 1.8 a.u., where the system energy has increased by 0.059 a.u. At this point ionization occurs and the hydrogen becomes H^+, leaving the CH_3 as CH_3^-. The H^+ is attracted to the extra charge center, so that by the point where the z coordinate has increased by 3.8 a.u. the system energy has actually decreased by 0.136 a.u. from the initial CH_4 case. Therefore this dissociation of $CH_4+Q \rightarrow CH_3^- + H^+ + Q$ proceeds exothermically with a barrier which is about 33% of the free CH_4 into CH_3+H dissociation energy.

Methane was chosen for this initial study due to its simplicity and high symmetry. In solid CH_4 the C atoms are at fixed lattice sites, whereas the four hydrogens on a given CH_4 unit rotate rather freely maintaining the CH_4 geometry. Thus CH_4 can orient readily. The CH_4 in the presence of a charge will orient as chosen for this study. Upon removal of a hydrogen in all cases, the resulting CH_3 or CH_4 fragment is unrelaxed. In actual practice such relaxations are important in obtaining quantitative values for dissociation, but are not going to modify the relative values for different pathways, which is the quantity of importance at present. For more complex systems such as CH_3NO_2 (nitromethane) or NH_4ClO_4 (ammonium perchlorate) the geometry of charge and molecule is a significant factor in the resulting behavior, where it is not for the more simple case of CH_4. The decision to place the point charges at a neighboring atom site was due to our assuming that (a) this is the closest it is likely to get in an actual system, and (b) the closer the charge, the greater its effect on the system. Of course we realize for a sheet of charge (surface charge) the electrostatic field is independent of distance. We do not expect to find actual cases with charge sheets of infinite extent, however.

There are other possible complications which were omitted here. These include the likely delocalization of charge on a charged defect, or the fact that the charged defect may itself be able to ionize rather than the neighboring entity. From the standpoint of definitive energy charges such effects are not negligible. We believe, however, that for simple preliminary studies this neglect is acceptable. First, the important charges we observe all occur while the molecular entity is still well separated from the point charge (5 a.u. or more) and thus the dominant effect of the defect is still due to its monopole field. Secondly, for the charged defect to ionize would require that the electron affinity of methane solid be greater than the ionization potential of the charged defect. This is possible; however, the electron affinity of solid methane seems to be a small fraction of an eV. Further studies are being performed on more interesting systems such as solids CH_3NO_2 and NH_4C10_4. The available results tend to fully confirm those of this preliminary study. These later studies will be incomplete for some time due to the complexity of the systems and the need for further refinements of the model which are in part detailed in this report.

IV. CONCLUSION

We have examined the possible role of charged defects on molecular solids in a series of simple, well-defined, but not exhaustive calculations. We believe the presence of charged defects is capable of inducing significant effects upon the molecular system. These effects are seen to be three in number. The first is that the presence of charge is capable of substantially altering the apparent or effective intermolecular interactions. The static induced polarization is seen to be able to generate effective molecule-molecule interactions which are increased by an order of magnitude or moreover the usual van der Waals case. The second is that the presence of a charge can increase the total energy of a molecular unit significantly. In such a case, however, some bonds strengthen and others weaken, at least when one constrains dissociation products to be charge neutral fragments. Thirdly, and perhaps most importantly, we find the charge able to reduce the barrier heights for molecular dissociation and, in one case studied, to induce exothermic dissociation into ionic fragments.

We believe this observed behavior may be significant to our understanding of the initiation of chemical reaction in energetic solids. In such systems, the molecules may interact weakly by van der Waals bonds but cooperate strongly in producing concerted reactions. Also in energetic systems, the dissociation of strong bonds may proceed exothermically or with a reduced barrier to dissociation in the presence of a charged defect.

These results, while significant, are still preliminary. Much further research is needed. Mechanisms for charging of nonionic systems need to be developed and, for ionic systems, need further refinement. Many cases need to be tested to demonstrate that this is a common mechanism or even a universal mechanism rather than only one of many mechanisms for modifying the intermolecular and intramolecular interactions in energetic solids. The possible effects of charge on gas-phase reaction also merit study. Finally, dynamic studies need to be performed on some systems to verify the total effect of such charge centers.

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[1] R. D. Bardo, in *Shock Waves in Condensed Matter,* edited by Y. M. Gupta, (Plenum, New York, 1985) p. 843; J. K. Dienes, in U. S. Office of Naval Research Workshop on Dynamic Deformation, Fracture and Transient Combustion [Chemical Propulsion Information Agency publication No. 404, p. 19 (unpublished)]; W. L. Elbau, R. G. Rosemeir, K. C. You, and R. W. Armstrong, *ibid.*, p. 81.

[2] G. E. Duval, in *Shock Waves in Condensed Matter,* edited by Y. M. Gupta (Plenum, New York, 1985); p. 1. Joint U. S. Office of Naval Research–Air Force Office of Scientific Research–Army Research Office Workshop Report on Fundamental Directions for Energetic Material Decomposition Research, p. 1 (unpublished); see also J. K. Dienes, in U. S. Office of Naval Research Workshop on Dynamic Deformation, Fracture and Transient Combustion, Ref. 1.

[3] S. F. Agnew, B. I. Swanson, L. H. Jones, and R. L. Mills, J. Phys. Chem. **89**, 1678 (1985).

[4] J. T. Dickinson, in U. S. Office of Naval Research Workshop on Dynamic Deformation, Fracture and Transient Combustion [Chemical Propulsion Information Agency publication No. 404, p. 153 (unpublished)].

[5] S. F. Coffey, in U. S. Office of Naval Research Workshop on Dynamic Deformation, Fracture and Transient Combustion, Ref. 4, p. 125.; in U. S. Office of Naval Research Workshop on Energetic Material Initiation Fundamentals [Chemical Propulsion Information Agency publication No. 406, p. 265 (unpublished)]; Phys. Rev. B **24**, 6984 (1981).

[6] M. I. Kornfel'd, Fiz. Tverd. Tela (Leningrad) **13**, 480 (1971) [Sov. Phys.—Solid State **13**, 387 (1971)]; N. A. T. Sal, I. M. Spitkovskii, and Yai A. Struk, *ibid* **24**, 2166 (1982) [**24**, 1233 (1982)]; S. G. Boeu and A. N. Galanov, *ibid.* **22**, 3069 (1980) [**22**, 1792 (1980)]; V. M. Finkel, Yu. I. Tyalin, Yu. I. Golovin, L. N. Muratova, and M. V. Gorsheneu, *ibid.* **21**, 1943 (1979) [**21**, 1116 (1979)]; L. B. Harris and J. Flasson, Solid State Commun. **38**, 1019 (1981).

[7] J. P. Hirth and J. Lothe, *Theory of Dislocation,* 2nd Ed., (Wiley, New York, 1982).

[8] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic*

Crystals, 2nd ed. (Dover, New York, 1948).

[9] N. F. Mott and M. J. Littleton, Trans. Faraday Soc. **34**, 485 (1938).

[10] P. Ho, M. E. Coltrin, J. S. Binkley, and C. W. Melius, J. Phys. Chem. **90**, 3399 (1986); **89**, 4647 (1985).

[11] A. B. Kunz, Philos. Mag. B **51**, 209 (1985).

[12] D. R. Beck and A. B. Kunz, J. Phys. B **17**, 2159 (1984).

[13] P. W. Goalwin and A. B. Kunz, Phys. Rev. B **34**, 2140 (1986).

[14] D. J. Thoules, *The Quantum Mechanics of Many Body Systems* (Academic, New York, 1961); E. R. Davidson and D. W. Silver, Chem. Phys. Lett. **52**, 403 (1977).

[15] A. B. Kunz, Phys. Rev. B **6**, 606 (1972).

[16] R. J. Bartlett, I. Shavitt, and G. D. Purvis III, J. Chem. Phys. **71**, 281 (1979); Y. S. Lee and R. J. Bartlett, Int. J. Quantum Chem. Symp. **17**, 347 (1983).

[17] L. Pauling, Proc. Soc. London, Ser. A **114**, 191 (1927).

[18] J. M. Farrar *et al.*, Chem. Phys. Lett. **19**, 359 (1973).