Computer Simulation of Defects in Ammonium Perchlorate*

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The electrical conductance of ammonium perchlorate has been theoretically investigated by a computer simulation technique using a polarizable point-ion model. The cohesive energy of the crystal was obtained from a Born-Harber cycle calculation. The Born-Mayer repulsive parameter was obtained from the crystal binding energy. The relaxation of approximately 50 ions was accounted for by exact calculation of the repulsive, electrostatic, and polarization energies. Twenty-one defect calculations were performed in all.

Based on these calculations, a novel turnstile mechanism involving slow synchronous rotations of the perchlorate ions to allow passage of ammonium ions is proposed for vacancy migration, which accounts for the high-temperature electrical conductance.

The energy of formation of a Schottky defect pair was calculated to be 1.66 eV, and the activation energy for migration of a vacancy was found to be 4.53 eV.

Introduction

Much of the fundamental work on the kinetics of the thermal decomposition of ammonium perchlorate has been extensively reviewed by Keenan and Siegmund (*1*), Hall and Pearson (*2*), and Jacobs and Whitehead (*3*). More recently, Herley and Levy (*4–7*) have made a detailed experimental study of some of the lattice imperfection, which shows the significant effect of dislocations on the rate of decompositions of ammonium perchlorate.

It has been known for a long time that the crystal structure of ionic solids plays an important role in their decomposition. Ammonium perchlorate is a white crystalline solid that undergoes a phase change at 240°C. The polymorphic change can be attributed to the onset of free rotation of the perchlorate ion (*1–3*). In the ammonium perchlorate lattice the ammonium and perchlorate ions act as independent species, and their ability to rotate freely has been the topic of much discussion. Early decomposition studies predicted the rotation of the ammonium and perchlorate ions above 240°C. The ammonium

ion was considered to rotate freely in the orthorhombic form as well. These conclusions were based solely on thermal decomposition data.

A structure comprised of an ordered, hydrogen-bonded arrangement of the NH_4^+ ions was suggested from early X-ray studies (*8*). This arrangement is not consistent with the overwhelming evidence from IR (*9*), EPR (*10*), NMR (*11*), slow neutron data (*12*), and neutron diffraction data (*13*), all which suggest the free rotation of the ammonium ion at room temperature.

One interesting feature of an ionic solid is the possibility of correlating the creation and destruction of charge carriers by measurement of the dc conductance during its thermal decomposition (*14*).

The role of point defects and their properties in alkali halides has been handled successfully using the classic Born point-ion model with modification to account for the polarization energy. This basic model was first employed by Mott and Littleton (*15*), later developed by Hatcher and Dienes (*16, 17*), and then extended by Dellin et al. (*18*).

The idealized picture of the ionic crystal was proposed by Born (*19*) for the purpose of evaluating the lattice energy of the crystal; as a conse-

quence of its success and simplicity, it has subsequently been applied to the description of other properties of ionic crystals. In the framework of this model, Benito et al. (20, 21) calculated the crystal lattice energy of the ionic crystal as composed of energy terms arising from the interaction between the ammonium and perchlorate ions. They also made similar calculations for the alkali perchlorates. In addition to the net binding energy provided by the electrostatic interactions of the pointlike charges of the ammonium and perchlorate ions, the bonding arising from a synchronization of the electronic motions in the complex ions is considered. The contribution of the van der Waals interactions is considered even though they are only of the order of a few percent of the crystal lattice energy. The attraction due to the mutually induced electronic dipoles was obtained as well as the zero point energy. These attractive crystal forces are balanced by the overlap Born repulsive forces. The Born repulsive energy is in fact a combination of several energy terms, i.e., the change in the energy of the ions going from the free state to the crystal state, the exchange interaction energy of the ions, and the corrective terms to the coulomb energy arising from deviations of the actual electron distribution assumed in the Madelung energy. Benito and Masia (21) obtained the Born repulsive energy contribution from compressibility data. The results of these calculations agreed surprisingly well with experimental data.

The migration of a vacant lattice site through the crystal of an alkali halide has been shown to account for its electrical properties. Wise (22) has found that the electrical conductivity of ammonium perchlorate is quite high as compared to the alkali halides. He has suggested a proton transfer mechanism based on his observation of increased electrical conductivity with the addition of ammonia gas. Wise suggested an effective ion transfer by the motion of a proton moving from an ammonium ion to an interstitial ammonia molecule. However, Maycock and Verneker (14) have suggested in a later study that the electrical conductivity in ammonium perchlorate can be attributed to a similar mechanism as in the alkali halides, the vacancy migration mechanism. It has been found that the electrical conductivity in ammonium perchlorate increases with the introduction of more defects, as would be expected if the mechanism were defect dependent (23). Ammonium perchlorate under-

goes a crystal structure change at approximately 250°C from orthorhombic to cubic. Wise, using pressed pellets, found no break from linearity in his conductivity measurements, whereas Maycock and Verneker (14), using single crystals of ammonium perchlorate, found a knee at 250°C and another at 280°C. The measurement of the ionic conductivity of ammonium perchlorate during the thermal decomposition has been used to follow the production and destruction of charge carriers (14). These charge carriers have been related to the defect structure of ammonium perchlorate and have been used to explain the thermal decomposition and several of the peculiar properties it exhibits (14). Ammonium perchlorate in the orthorhombic form decomposes only 30%, leaving a residue of pure ammonium perchlorate, whereas in the cubic form decomposition is complete (1–3). Activation energies of 1.38 eV for the formation of defects in ammonium perchlorate have been determined experimentally by Wise (22) over the range 220°–320°C for pressed pellets. Maycock and Verneker (14) obtained a value of the order of 2.0 eV at 255°–280°C and 5.6 eV at 280°–350°C.

The intent of the present work is to investigate the role of a variety of defects which may account for the electrical conductance and be influential in the mechanism for thermal decomposition.

Theoretical Model

Most defect calculations are performed on a static lattice in a manner similar to cohesive energy calculations. The defect properties are obtained from the difference between two different static configurations, e.g., the energy of a cation interstitial is equal to the energy of the defect crystal minus the energy of the perfect crystal. The energies so obtained are presumed to be equal to the corresponding enthalpies in a solid, which is in thermodynamic equilibrium above room temperature. In order to justify this assumption, one must consider the crystal at high enough temperatures for the classic equipartition to hold. Assuming a harmonic potential energy function about the configuration specified in the static lattice, then the defect enthalpy is equal to the corresponding static lattice energy at these temperatures. This assumption is commonly made in most defect calculations (16, 17). In general, the defect entropies are ignored. This approximation appears to be

quite satisfactory in practice and will be made in the defect calculation on ammonium perchlorate.

Despite the simplicity of the model, the interactions developed give a reasonable simulation of the ammonium perchlorate crystal. Depending on the symmetry of the defect, the ions may be grouped into various shells in which the ions have similar displacements and dipoles. This simplifies finding the minimum energy configuration and reduces the computer time needed to solve the set of simultaneous linear equations.

The method of the defect calculation is based on the physical model, which has already been discussed in the introduction. Even though this physical model is fairly simple, the computations necessary to obtain numerical values of defect energies are rather complex and involve computer simulation techniques. These calculations, although not lending themselves to simple analytical expressions, are very useful for predicting properties of defects not easily attainable experimentally.

The expression for the various energies involved in the total crystal lattice energy of the defect crystal relative to the perfect crystal is made up of several parts,

$$E = E_S + E_P + E_R \tag{1}$$

where E is the energy of formation of the defect, E_S is the electrostatic energy of the defect crystal, E_P is the polarization energy of the defect crystal, and E_R is the repulsive energy of the defect crystal, all relative to the perfect crystal. Calculations of E in the static lattice include the contributions of the coulomb, overlap, and polarization energies, but neglect the van der Waals forces.

The electrostatic energy can be calculated exactly from

$$E_S = \Sigma'_{ij}(e_i e_j/r'_{ij} - e_i e_j/r_{ij}). \tag{2}$$

The prime notation over the summation sign indicates that the sums $i = j$ are neglected. Here e_i and e_j are the charges on ions i and j, r'_{ij} is the perfect crystal interionic spacing between ions i and j, and r'_{ij} is the spacing between ions i and j in the defect crystal.

Several methods have been developed to produce a rapid convergency of this sum. Historically the Ewald method (24) has been employed. However, a more economical modification (25) is used in the present work.

In order to calculate the polarization energy, one must consider the total electric field at ion i in

the crystal caused by the dipoles and the monopoles acting on it. This is given by

$$E_i^{tot} = E_i^{chg} + E_i^{dip}. \tag{3}$$

In general the induced electronic dipole on ion i is (26)

$$
\begin{aligned}
P_i &= \alpha_i E_i^{tot} \\
&= \alpha_i E_i^{chg} + \alpha_i E_i^{dip} \\
&= \alpha_i E_i^{chg} + \alpha_i \Sigma_j[3r_{ij}(p_j' \, r'_{ij})/r'^{5}_{ij}] - (p_j/r'^{3}_{ij}) \quad (4)
\end{aligned}
$$

The above equation is true for all dipoles in the crystal, and, therefore, we can set up a system of simultaneous linear equations. In this matrix one can solve for the individual dipoles summed over j by using a standard numerical scheme.

The polarizability of the ammonium ion was taken from the literature (27). The polarizability of the perchlorate ion was calculated from the Lorenz-Lorenz equation (26).

The polarization energy may be obtained by substituting the induced electronic dipoles into the following equation:

$$E_p = -\tfrac{1}{2} \Sigma_i p_i E_i^{chg} \tag{5}$$

where the sum is over all the polarizable ions in the crystal.

The repulsive energy in pure ammonium perchlorate lattice is given by (24)

$$E_R = \Sigma'_{ij}(b \exp(-r'_{ij}/\rho) - b \exp(-r_{ij}/\rho). \tag{6}$$

Here the prime notation has the usual meaning. The constant b was taken to be 0.338×10^{-12} erg from the work of Fumi and Tosi (28, 29).

Benito and Masia (20, 21) have determined the lattice energy of ammonium perchlorate at room temperature to be 143.8 kcal/mole. Ammonium perchlorate undergoes a polymorphic transformation from the orthorhombic to the cubic form at 240°C with an enthalpy change of 2.3 kcal/mole (1). Making this correction but neglecting other temperature effects, one can calculate an approximate lattice energy for the cubic crystal of 141.5 kcal/mole or 6.1 eV.

Rho was found to be 0.336 A from the above calculation. The repulsive interactions in Eq. (6) are made up of the Born-Mayer two-body central forces of the form $b \exp(-r_{ij}/\rho)$. In the case of foreign ions in the ammonium perchlorate crystal lattice, these repulsive interactions are taken to be the same as in the pure crystal.

In crystals that contain substitutional ions or foreign interstitial species, one must account for the repulsion interactions due to the foreign ion

or atom interaction with the host lattice. As a first approximation, these interactions are assumed to be the same as in the host lattice. This approximation is fairly good when the size and nature of the foreign species is closely related to the host species (25). However, when the interactions are between large ions such as the ammonium and perchlorate ions and small ions like lithium and helium, the validity of the approximation is in doubt.

Results and Discussion

The sensitivity of the results to a change in the model of ammonium perchlorate used was investigated and the effects of the changes are summarized in Table I. Case A is the model used in the present study. In case B and C the parameter ρ was varied by $\pm 10\%$. In case D and E the repulsive interactions were calculated from compressibility data of the orthorhombic crystal (28, 30). Results of the sensitivity check indicate that there is very little change in the activation energy of migration, even though large changes in the repulsive parameters are made. The energy of formation of the positive and negative ion vacancies appears to change substantially with these same changes in the repulsive parameters. Cases D and E give unrealistic energies of formation of the Schottky pair. Therefore, these parameters were not considered further. Case A was used throughout the rest of the calculations as it gives the most realistic value for the energy of formation of the Schottky pair. This Schottky energy is probably the most interesting parameter by means of which to judge an ionic crystal model and has been the one most thoroughly investigated. It is calculated as the sum of the formation energies of positive and

TABLE I

VARIATION IN THE REPULSIVE PARAMETERS

	Parameters		Vacancy		Activation energy (eV)
Case	ρ	b	+	−	
A	0.336	0.338	3.807	3.861	4.52
B	0.370	0.338	3.75	—	4.58
C	0.302	0.338	3.80	—	4.53
D	0.404	0.440	0.830	3.69	7.50
E	0.240	0.837	1.12	−0.543	7.21

TABLE II

DEFECT CALCULATIONS IN AMMONIUM PERCHLORATE

Type	Energy (eV)	
	Before relaxation	After relaxation
1. − Ion vacancy	4.193	3.861
2. + Ion vacancy	4.055	3.807
3. Migration − ion	67.124	46.272
4. Migration + ion	15.218	8.334
5. NH^+_4 Body centered	2.494	1.349
6. NH^+_4 Face centered	10.545	3.266
7. ClO^-_4 Body centered	49.904	7.225
8. ClO^-_4 Face centered	—	9.978
9. Divacancy	6.175	6.000
10. Dinegative vacancy	10.933	10.135
11. Dipositive vacancy	11.002	10.292
12. Quadrivacancy	10.937	10.628
13. 110 Interstitial saddle point	61.620	7.132
14. 111 Interstitially split saddle point	6.587	4.90

negative ion vacancies minus the binding energy per ion pair.

Twenty-one individual defect calculations were made using the model described earlier. The defect calculations on pure ammonium perchlorate are given in Table II. The energy before relaxation refers to the original rigid lattice with no allowance having been made for distortion of lattice parameters by the defect. The energy after relaxation refers to the state where the lattice has relaxed to its minimum energy as a result of distortion caused by the defect. This minimization procedure has been described by Hatcher and Dienes (17).

In Table III the activation energies for migration of various defects in ammonium perchlorate

TABLE III

ACTIVATION ENERGIES FOR DIFFUSION IN AMMONIUM PERCHLORATE

Species	Direction	Activation energy (eV)
Cation vacancy	110	4.527
Anion vacancy	110	42.441
NH^+_4 Interstitial	110	5.783
NH^+_4 Interstitial	100	1.917
NH^+_4 Interstitial	111	3.55

TABLE IV

FOREIGN ION DEFECT CALCULATIONS IN AMMONIUM PERCHLORATE

Species	Foreign Ion Energy (eV) After Relaxation	Body center	Face center
K^+	−0.4931	0.35711	2.121
Na^+	−1.2124		
Li^+	−1.5238	−2.2680	−1.6723

are listed. These activation energies have been calculated from Table II. The foreign ion defect calculations are compiled in Tables IV and V.

From these tables it is noted that the Li^+ interstitials have the lowest activation energy for migration of all the interstitial species studied. This fact is not especially surprising as the Li^+ ion is small and has a tightly bound charge distribution. Similar results were obtained for cation diffusion in alkali halides (31) and Li^+ ion diffusion in LiH (18).

It can be shown from the use of the present model that the electrical conductance in ammonium perchlorate is ionic. The migration of a vacancy accounts for the conductivity just as has been shown in alkali halides (32, 33). A value of 4.5 eV was obtained in the present work for the migration of a positive ion vacancy in the 110 direction. This energy of migration of a vacancy in ammonium perchlorate is taken to be the activation energy for the migration process, assuming that the process illustrated in Fig. 1 is the rate-determining step for the activation energy. This same assumption has been made by other investigators (16–18, 34). At temperatures from 250° to

TABLE V

ACTIVATION ENERGIES FOR FOREIGN ION MIGRATION IN THE LATTICE

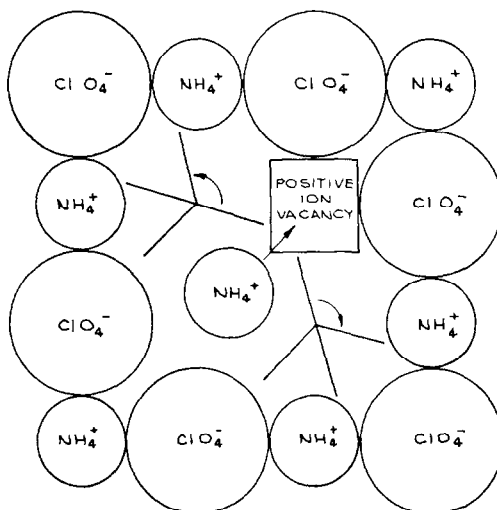| Species	Activation energy from substitutional to body centered position (eV)	Activation energy from body centered to face centered Position (eV)
K^+	+4.651	1.764
Na^+	—	—
Li^+	+3.063	0.596

FIG. 1. Ammonium ion shown migrating through perchlorate ion turnstiles in 110 direction, leading to diffusion of a positive ion vacancy.

280°C Maycock and Verneker (14) obtained an activation energy of the order of 2.0 eV, which is their suggested energy of formation of a Schottky pair. Based on comparison with these experimental results, it appears that there is another rate-determining process involved in the activation energy. The present model of ammonium perchlorate gives an energy of formation for a Schottky pair as 1.65 eV.

In order to explain the diverse experimental and theoretical results concerning the migration of a vacancy in ammonium perchlorate, one must look for another mechanism. A mechanism based on the effect of asymmetry of the perchlorate ion just above the transition point has been suggested (34). This mechanism can also account for the exceptionally high conductance between 250° to 280°C and the sudden increase in activation energy above 280°C. Assuming that the perchlorate ion is rotating at a much lower frequency than the vibrational frequency of the crystal, it is possible that the perchlorate ion is not an effective spherical unit even though the ammonium ion may be so. It can be seen from Fig. 1 that if the perchlorate ion is a spherical unit, it will take considerable energy, i.e., 4.5 eV, for the ammonium ion to migrate into the vacancy along the 110 direction. However, it is possible that the ammonium ion can pass through a slowly rotating perchlorate ion in a low energy configuration as illustrated in Fig. 1. In a preferred orientation of the perchlorate ion

the ammonium ion can pass through by a turn-stile mechanism giving rise to the low activation energy of conduction below 280°C.

It is unlikely that interstitial conductance of NH_4^+ is important at these temperatures because the energy of formation of a Frenkel defect is so much larger than that of the Schottky defect, namely, 4.05 eV compared to 1.65 eV, respectively. The energy of migration of the ammonium ion interstitial is 1.20 eV. This mechanism is also illustrated by Fig. 1. The energy of migration is taken to be the activation energy is one assumes that the migration process in Fig. 1 is the rate-determining process.

The binding energy of a divancy is 1.67 eV, and it would be stable if formed. Assuming the divacancy is stable, the activation energy for the divacancy migration would be approximately 2.0 eV as compared to 4.5 eV for the positive ion vacancy migration. These results indicate the feasibility of the turnstile mechanism.

The denegative and dipositive vacancies are both unstable with binding energies −2.47 and −2.63 eV, respectively. The formation of quad-rivacancies is favorable by 1.37 eV.

The computer experiments performed on pure and doped ammonium perchlorate are by no means exhaustive; however, based on the results of the computer simulation and the experimental results discussed, a mechanism for the ionic conduction has been proposed. As has been mentioned, the activation energy for migration of an interstitial in ammonium perchlorate would probably be high because of the large energy of formation of the Frenkel pair and therefore would not play a significant role in the process.

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