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REVIEW: MECHANISM OF LOW-TEMPERATURE THERMAL DECOMPOSITION OF AMMONIUM PERCHLORATE

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Ammonium perchlorate, an oxidizer extensively used in solid propellant and explosive formulations, exhibits unusual thermal decomposition behavior that is still not completely understood. At low temperatures (<300°C), ammonium perchlorate undergoes incomplete thermal decomposition, resulting in partial mass loss and leaving behind a porous solid residue that can undergo violent combustion upon ignition. Understanding low-temperature thermal decomposition of this material is challenging, because the process is driven by a network of solid-phase, gas-phase, and surface reactions whose dynamics depend on physical properties such as particle size, exposed surfaces, and crystal defects. This paper presents a review of recent and historical work on the mechanism of thermal decomposition of ammonium perchlorate, and is organized in order to clearly describe the various aspects of the thermal decomposition process, highlight aspects of this problem that are well-characterized, and expose gaps in our understanding of the decomposition process where more work is needed. This review is therefore simultaneously a reference guide for researchers using this material in practical application, and an account of current understanding to facilitate the development of a complete physical and chemical mechanism for the decomposition process.

I. INTRODUCTION

Thermal decomposition of ammonium perchlorate (AP) has been studied extensively for many decades due to its widespread use as an oxidizer in solid propellants. Of particular interest to energetic materials research is the thermal decomposition of AP at low temperatures (below approximately 300°C), a complex process that is still not mechanistically well understood. At low temperatures, AP decomposes incompletely, slowly releasing various decomposition gases and leaving behind a microporous solid residue. The decomposition process is driven by a combination of physical and chemical phenomena, and its evolution depends sensitively on a variety of material-dependent factors, such as particle size, crystal defects, and impurities.

The physical and chemical complexity of the decomposition process, coupled with its sensitivity to sample characteristics, has hindered the development of a complete, detailed physical/chemical mechanism that explains all aspects of the process. Direct measurements of many of the relevant processes simply have not been possible, often forcing inferences from indirect measurements. The sensitivity of the decomposition process to sample properties has made it difficult to compare results from different investigations. To date, many investigations have examined various aspects of the decomposition process, and several publications have hypothesized compelling physical/chemical mechanisms. Several reviews have summarized this body of work [1-3]. At present, however, no particular mechanism has been proven, and many hypotheses regarding the details of the decomposition process remain unverified.

The goal of this review is to capture and compile the most important and most conclusive details from the literature on the physical and chemical processes involved in the low-temperature thermal decomposition process, with the goal of aiding the development of a comprehensive mechanism. As such, this review is not intended to be a comprehensive guide to the entire literature on ammonium perchlorate, but rather a guide to the subsection of the literature that addresses mechanistic details, and a definitive guide to the low-temperature decomposition process. It is hoped that this review will be a valuable resource for researchers

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studying thermal decomposition of ammonium perchlorate and other solids, as well as formulation chemists who use ammonium perchlorate in the development of propellant and explosive formulations.

II. CRYSTAL STRUCTURE OF AMMONIUM PERCHLORATE

Ammonium perchlorate is a transparent crystalline material, and adopts an orthorhombic crystal structure (space group $Pna2_1$) at ambient conditions, with unit cell parameters a = 9.227 Å, b = 7.454 Å, and c = 5.819 Å [4]. At 240°C, AP adopts a cubic crystal structure with a = 7.63 Å [5]. Under hydrostatic compression at room temperature, ammonium perchlorate undergoes two phase transitions at approximately 0.9 GPa and 3.0 GPa [6], although the crystal structures of these new phases are not precisely known. Commonly-observed crystal faces of the orthorhombic structure are shown in Figure 1, along with their Miller indices.

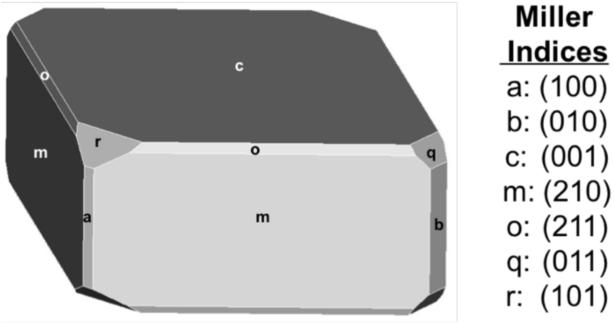

Figure 1: Crystal faces of orthorhombic ammonium perchlorate. (Courtesy W. Erikson [41])

III. OVERVIEW: LOW-TEMPERATURE THERMAL DECOMPOSITION

The detailed kinetics of the low-temperature (<300°C) thermal decomposition of ammonium perchlorate depends on a variety of factors (particle size, confinement, presence of defects and impurities, etc.) but the general process is characterized by the presence of three sequential stages [1,2,7,8]:

(i) *Induction Stage:* The initial phase of decomposition, or “induction” stage, is characterized by localized reaction at defects within the crystal and/or near its surfaces. During this stage, evolution of gaseous products and loss of sample mass are minimal; reaction appears to occur entirely within the crystal volume. The duration of this stage of the decomposition depends strongly on temperature and may last tens of minutes to many hours.

(ii) *Acceleratory Stage:* The induction phase is followed by an acceleratory stage, during which the reaction accelerates, gaseous products are evolved from the sample, and the majority of mass loss occurs. Observed decomposition products include H_2O, O_2, Cl_2, N_2O, NH_3, $HClO_4$, HCl, NO_2, N_2, NO, and ClO_2. At this stage, the crystal becomes increasingly porous, with numerous channels formed throughout.

(iii) *Deceleratory Stage:* During final stage of decomposition, or “deceleratory” stage, decomposition slows and ceases, and remains incomplete. The final extent of decomposition typically ranges from 5% to approximately 30%, leaving behind a porous residue of pure ammonium perchlorate.

Phases of the decomposition process are illustrated in Figure2. The kinetics of the decomposition process depend sensitively upon the following factors:

- *(i)* Confinement and pressure;
- *(ii)* Particle size and morphology;
- *(iii)* Presence of chemical impurities;
- *(iv)* Crystal defects.

All of the above can have dramatic effects on the kinetics of the various stages of decomposition, as well as the overall extent of decomposition of the solid.

Observable decomposition has been noted at temperatures as low as 130°C [2,9]. The kinetics of the thermal decomposition process in the orthorhombic phase differ from the cubic phase, but the general features of the process are similar [7, 10, 11].

Above ~380°C, the high-temperature decomposition process occurs. The high-temperature decomposition process is distinct from the low-temperature decomposition process in that it (*i*) lacks an induction period (*i.e.* occurs promptly) and (*ii*) proceeds to completion, leaving no solid residue [7-9]. These two observations delineate the low-temperature and high-temperature decomposition regimes as clearly distinct chemical processes. The transition from low-temperature to high-temperature decomposition is not sharp, and occurs between ~300-380°C [12].

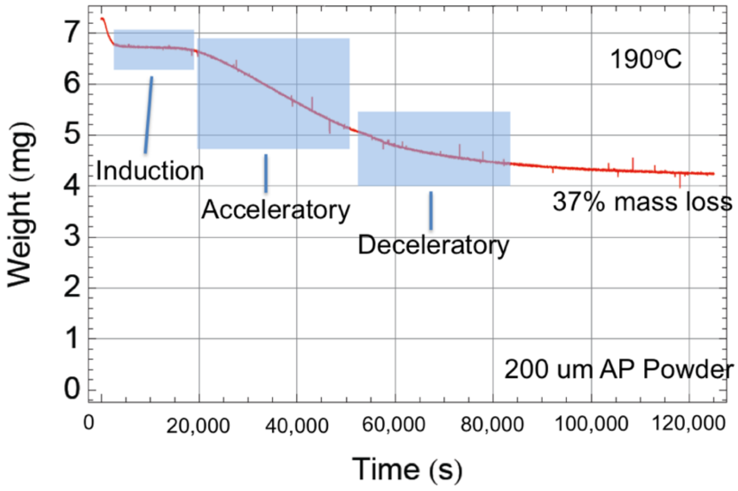

Figure 2. Thermogravimetric data illustrating mass loss observed during decomposition of 200 μm AP powder at 190°C. Phases of decomposition are noted.

IV. DECOMPOSITION PRODUCTS

The low-temperature decomposition of ammonium perchlorate produces a number of product species whose relative rates of production depend on a variety of parameters (including temperature, time, and confinement), and properties of the sample (including particle size, shape, chemical purity, and the presence of intentional additives). The confinement of the sample, for example, has a strong effect on the evolution of the reaction process [10,13,14]; under confined conditions, the product decomposition gases remain in contact with the decomposing solid, causing secondary reactions that do not occur when the sample is decomposed in vacuum. The sensitivity of the decomposition process to so many variables concerning the sample and its environment has resulted in differences between analyses of product gases, particularly in early investigations [2,15].

While the quantitative kinetic aspects of the low-temperature decomposition process depend on many factors, the decomposition process invariably produces the same set of products. The major decomposition products are H_2O, O_2, N_2O, and Cl_2; minor decomposition products include N_2, NO_2, NO, HCl, and ClO_2 [10,13,14-21]. Depending on temperature and confinement, NH_3 and $HClO_4$ may be observed as minor or major decomposition products [10,13,14]; these species are produced by dissociative sublimation, which occurs in parallel with decomposition of the solid. Other trace products, such as ClO and ClO_3 [10] have also been reported.

It is important to note that the molar ratios of all of these products depend on temperature, pressure, and extent of reaction. The decomposition of ammonium perchlorate is a complex physical and chemical process, and it is not possible to write a single equation that accounts for the decomposition process appropriately for all conditions [7,10,13,14,17].

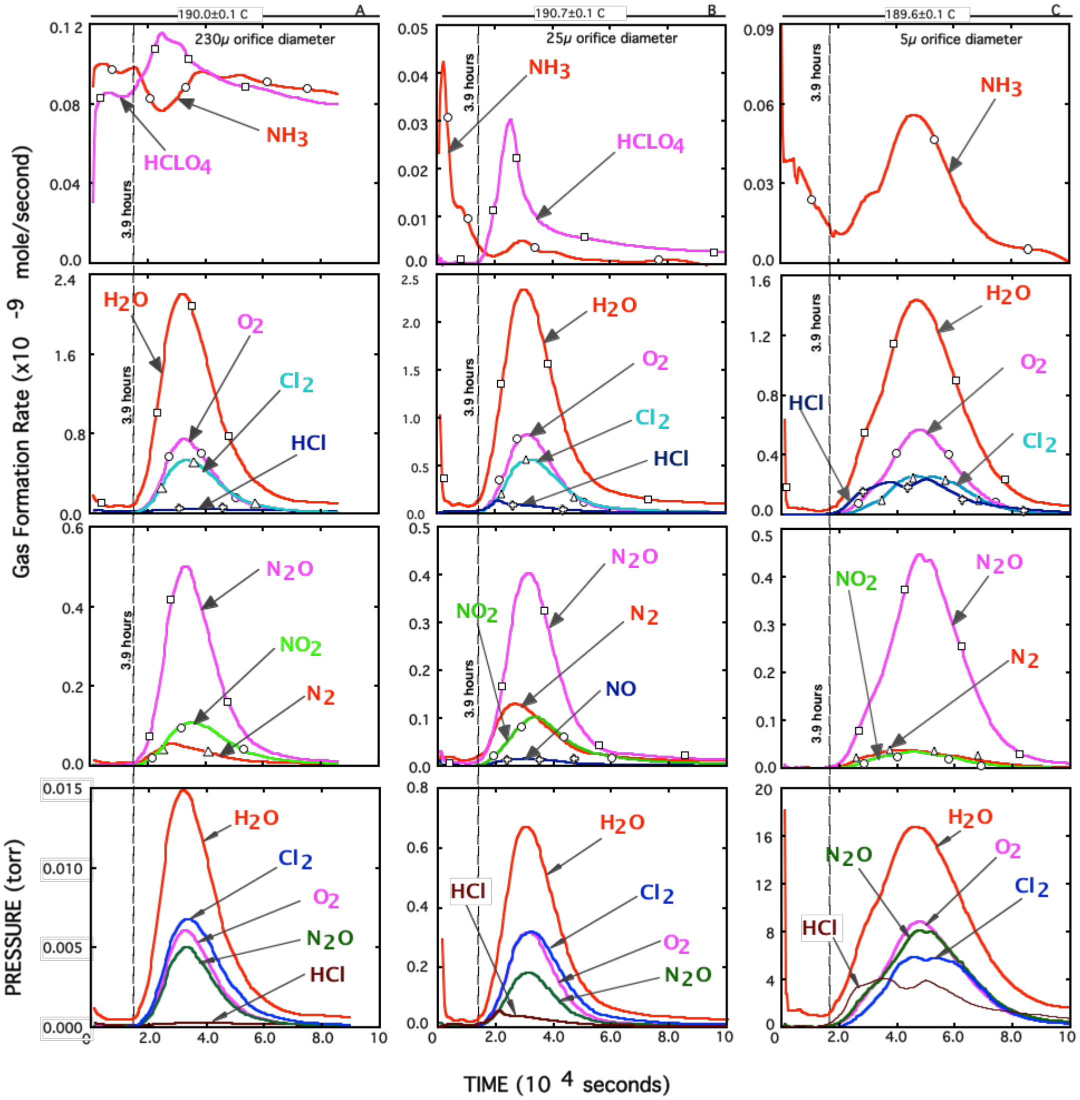

Figure 3. Decomposition products from decomposition of ammonium perchlorate powder at 190°C, and their dependences on retained product gas pressure. Column A corresponds to a pressure of 0.015 torr, Column B corresponds to 0.7 torr, Column C corresponds to 15 torr. (Courtesy L. Minier [14])

V. GENERATION AND EVOLUTION OF POROSITY

A hallmark of the low-temperature decomposition process is the development of microscopic porosity in the decomposing crystalline solid. Thermal decomposition begins at localized sites and progresses through the solid, generating microscopic channels as the reaction progresses, and leaving behind a porous solid as the decomposition process ceases. The evolution of porosity during the decomposition process has been examined both for single crystals and powdered ammonium perchlorate, and notable differences in the progression of the decomposition process have been observed.

(*i*) *Evolution of porosity in single crystals*

Several investigations have observed the evolution of porosity in single crystals of ammonium perchlorate [8, 22-25]. Decomposition begins with the formation of small pits on or just below the surface of the crystals [23-25]. The pits deepen to become channels, typically 1-2 μm wide with a square cross-section, and progress inward toward the interior of the crystal. The channels become interconnected as the decomposition process progresses [25]. The progression of channels inward forms a roughly uniform decomposition front, parallel to the crystal surfaces, that propagates toward the center of the crystal [8, 23]. The decomposition process has also been shown to progress inward along particular crystallographic directions, particularly from the *m* face along the [010] direction (i.e. towards the *b* face), leading to the appearance of "bands" of decomposed product [23,24]. The decomposition process ceases when the progressing reaction fronts meet at the center of the crystal. Figure 4 shows electron microscope images of partially-decomposed AP single crystal samples.

(*ii*) *Evolution of porosity in powders*

The evolution of porosity in particles of ammonium perchlorate powder has also been investigated [13,14,21,26]. The powder particles, unlike single crystals employed in the studies above, are smooth, round, polycrystalline, and contain larger defects such as voids. Like single crystals, decomposition is observed to begin at or near the particle surface, forming small pits during the early stages of the decomposition process. Unlike single crystals, however, decomposition simultaneously begins in the interior of the particle, near the interior surfaces of voids [13]. Microscopic channels develop both at the exterior particle surfaces and interior void surfaces, which become interconnected and form reacting fronts that simultaneously progresses inward from the particle surfaces and outward from the interior defects. The progression of the reaction fronts inward from the surface of the particle and outward from the defects is not perfectly radial; the fronts progress faster in some directions than others, presumably due to the imperfect nature of the powder particles.

A recent investigation by Kalman *et al.* [26] followed the decomposition of large powder particles using nano-computed tomography, and found that decomposition originates just approximately 15 micrometers below the exterior surface of the particles.

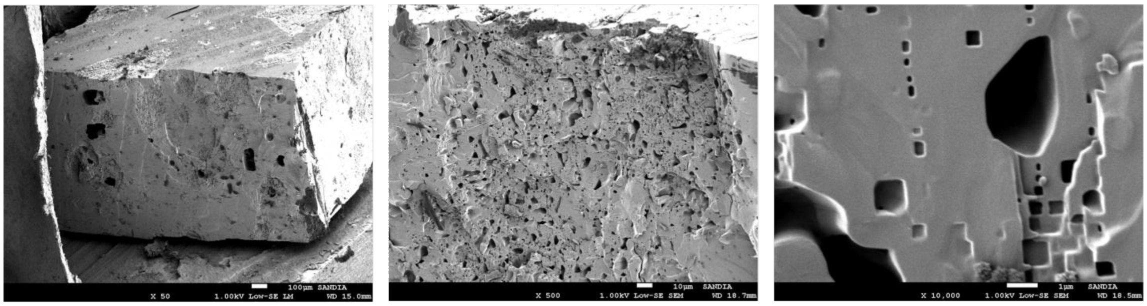

Figure 4. Scanning electron microscope images of partially-decomposed single crystals of ammonium perchlorate, illustrating extensive porosity.

VI. EFFECTS OF CONFINEMENT AND PRESSURE

The low-temperature decomposition of ammonium perchlorate produces a number of product species whose relative rates of production depend on whether the sample and its decomposition products are retained (or "confined") together during decomposition. Without confinement, gaseous decomposition products freely leave the sample as they are produced, leading to enhanced sublimation of the solid [7,8,12,13,27,28]. Under confined conditions, gaseous decomposition products remain in contact with the decomposing solid, suppressing sublimation of the solid AP, and also causing secondary reactions that do not occur when the sample is decomposed in vacuum or in a flowing inert atmosphere [10,13,14].

The presence of a static inert atmosphere has been shown to suppress sublimation [7, 12], and promotes decomposition [12].

(i) Effect on dissociative sublimation

Dissociative sublimation of ammonium perchlorate, summarized by the reaction

$$\mathrm{NH_4ClO_4}(s) \leftrightarrow \mathrm{NH_3}(g) + \mathrm{HClO_4}(g) \qquad (1)$$

occurs in parallel with decomposition of the solid. The process is reversible; recombination of the NH_3 and $HClO_4$ gases on the surface of the solid, or on walls of a containing vessel, will reform solid ammonium perchlorate. Heating AP in vacuum allows the NH_3 and $HClO_4$ gases to escape, and results in gradual (and complete) sublimation of the solid. Heating in a closed vessel retains the NH_3 and $HClO_4$ gases, which allows the establishment of equilibrium in Eq. (1) and prevents full decomposition of the solid by dissociative sublimation [27,28]. The presence of an inert atmosphere likewise suppresses dissociative sublimation [7,12]. The dissociative sublimation process occurs even after the low-temperature decomposition process is complete [12,27]. The kinetics of dissociative sublimation in ammonium perchlorate has been examined and characterized extensively over a range of temperatures and pressures by Jacobs and Russell-Jones [28].

(ii) *Secondary reactions*

Confinement of the gaseous decomposition products promotes secondary reactions, both between the decomposition gases and the unreacted solid, and among the decomposition gases themselves [10, 13]. These secondary reactions affect the kinetics of the decomposition process, and the relative ratios of the decomposition products, but do not appear to lead to production of different gas-phase products [13]. In terms of kinetics, Minier and Behrens observed no effect of confinement on the induction period, but an increase in the length of the acceleratory period with confinement, and a decrease in the decomposition rate during the deceleratory period with confinement. In terms of decomposition product ratios, Minier and Behrens observed decreases in production of Cl_2 and $HClO_4$, and increases in production of HCl and NH_3, relative to the other product gases, when the decomposition gases are confined to interact with the sample.

VII. EFFECTS OF PARTICLE SIZE AND MORPHOLOGY

The particle size and morphology of ammonium perchlorate affect the kinetics of the decomposition process and final extent of reaction. These effects have been examined using ground single crystals, recrystallized ammonium perchlorate, and industrially-manufactured powders of varying particle size. It should be noted that the method of preparation can impart properties to the material that are known to affect the decomposition process (for example, the mechanical stress of grinding crystals introduces dislocations and other crystal defects; recrystallization tends to reduce impurities in the material). It is therefore difficult to quantitatively compare results between studies that use samples prepared by different methods, and reliable quantitative comparisons can only be made within a given study.

(*i*) *Ground single crystals*

Bircumshaw and Newman [8] investigated the effect of particle size on decomposition rates in samples produced by grinding single crystals of ammonium perchlorate. They examined the decomposition of eight powders, with average particle diameters ranging from ~60 μm to ~190 μm, in isothermal experiments at 230°C. They observed little variation in the length of the induction period, but significant variation in the decomposition rate during the acceleratory period. The decomposition rate during the acceleratory period increased as the average particle diameter increased from ~60 μm to ~114 μm, and decreased as the particle diameter increased from ~114 μm to ~190 μm.

(*ii*) *Recrystallized ammonium perchlorate*

Pai Verneker and Maycock [29] investigated the effect of particle size on decomposition rates by isothermally decomposing recrystallized ammonium perchlorate samples with varying particle sizes. They examined the decomposition of four powders, with average particle diameters ranging from ~20 μm to ~110 μm, in isothermal experiments at 235°C. They observe similar induction periods for the different powders, with variation in the rate of decomposition during the acceleratory period. The decomposition rate increases as the particle size increases from ~20 μm to ~60 μm, and is slightly lower for the ~110 μm powder.

(*iii*) *Powders*

Mass loss and chemical species produced by thermal decomposition of industrially-manufactured ammonium perchlorate powders were examined in experiments by Minier and Behrens [13], using powders with three particle size distributions (~50 μm, ~200 μm, and ~500 μm). The powders were decomposed isothermally under relatively high confinement at 190°C. They observed similar induction periods for all three powders, but variation in mass loss rates during the acceleratory period as well as variation in the total mass loss. Mass loss rates during the acceleratory period and total mass loss (~33%) were comparable for the ~200 and ~500 μm powders, but slower mass loss and lower total mass loss (~23%) were observed for the ~50 μm powder. The decomposition gases and their production rates show similar behaviors: comparable gas production rates for the ~200 μm and ~500 μm powders, but lower gas production rates for the ~50 μm powder.

Atwood *et al.* [21] examined weight loss in similar powders, as well as smaller-particle samples of ground powder. They observed 34-35% total mass loss for both ~85 and ~300 μm powders, and less total mass loss for ground powder samples (~29% for ~85 μm ground powder, ~20% for ~30 μm ground powder, and 0% for ~3 μm ground powder). Atwood *et al* note that the ~3 μm powder did not appear to undergo decomposition, and only appeared to lose mass due to sublimation.

VIII. EFFECTS OF CHEMICAL IMPURITIES

Impurities present in ammonium perchlorate, either intentionally as an additive or unintentionally as a byproduct of preparation, can strongly affect the kinetics of the low temperature decomposition process. The effects of a wide variety of dopants and additives have been extensively examined in studies so numerous that they could constitute an entire review article on their own. Only the roles of those additives and impurities that may play an important role in the decomposition mechanism of AP are discussed here; for others, readers are referred to previous review articles [1-3]. The effects of (*i*) chlorate impurities, (*ii*) nitrate impurities, (*iii*) chloride impurities, and (i*v*) water content.

(i) Chlorate impurities

The effects of chlorate impurities are of particular importance, as chlorate ions (ClO_3^-) are common impurities in ammonium perchlorate samples. Khairetdinov and Boldyrev [30] reported a series of measurements on multiply-recrystallized AP (up to 5x), in which they quantified the amount of chlorate present in the sample after successive recrystallizations and quantified the characteristics on the induction period observed during thermal decomposition. The rate of nucleation and maximum number of surface nuclei both decrease with decreasing ClO_3^- concentration, and length of the induction period increases with decreasing ClO_3^- concentration.

Guillory, Mack, and King [31] investigated the thermal decomposition of pure ammonium chlorate, and showed that observable decomposition begins at approximately 75°C. The authors report the production of significant quantities of N_2, H_2O, HNO_3, and Cl_2, and smaller quantities of NH_3, ClO_2, N_2O, and HCl. The observation of decomposition at a temperature much lower than that of ammonium perchlorate may explain the above effects of chlorate ions on the induction period of AP.

(ii) Nitrates

Nitrate compounds have been shown to promote thermal decomposition of ammonium perchlorate. Bircumshaw and Newman [7] report that addition of ammonium nitrate to the ammonium perchlorate decreased the induction period by as much as 50%. Galwey and Mohamed (1984a, 1984b) showed that the addition of NH_4NO_3, KNO_3, $AgNO_3$, $BaNO_3$, $Mg(NO_3)_2{\bullet}6H_2O$, $Ni(NO_3)_2{\bullet}6H_2O$, $Cu(NO_3)_2{\bullet}6H_2O$ all promoted decomposition by reducing the induction time and increasing the decomposition rate.

(iii) Chlorides

Bircumshaw and Newman [7] report that addition of a small (1/250 wt%) addition of ammonium chloride lengthened the induction period by 10 minutes (~25%) at 230°C.

(iv) Effects of water content

The presence of water has been shown to affect the low-temperature decomposition process in AP. Water is invariably present in water-recrystallized AP. The effect of water on the low-temperature decomposition process has been studied by Galwey, Herley, and Mohamed [32], who compared the decomposition kinetics of water-recrystallized AP (empirical formula determined to be $(NH_4)^+_{0.87}\,(H_3O)^+_{0.17}ClO_4^-$) and anhydrous AP (empirical formula determined to be $(NH_4)^+_{0.95}(H_3O)^+_{0.05}ClO_4^-$) prepared by direct reaction of dry NH_3 and $HClO_4$ gases. The authors showed that induction time for decomposition of the water-recrystallized AP was approximately twice as long as anhydrous AP at 230°C (60 min vs. 30 min), and its decomposition rate was faster, indicating that the presence of water slows the decomposition process.

IX. EFFECTS OF DECOMPOSITION GASES

Low-temperature decomposition of ammonium perchlorate in the presence of select decomposition gases has been investigated in several works. Stevlov and Koroban [33] have shown that decomposition in the presence of Cl_2 gas decreases the length of the induction period and increases the decomposition rate during the acceleratory period. $HClO_4$ similarly shortens the induction period. Svetlov and Koroban also showed that exposure to oxides of chlorine (ClO_2, ClO_3) accelerates decomposition of AP. Khairetdinov and Boldyrev [30] also reported that exposure to ClO_2 significantly reduced the induction time.

Interestingly, immersion in ammonia gas appears to inhibit decomposition. Davies, Jacobs, and Russell-Jones [27] reported that decomposition in the presence of ammonia vapor lengthened the induction period, decreased the decomposition rate, and decreased the overall extent of decomposition. The presence of ammonia also inhibited post-decomposition sublimation. Jacobs and Pearson [34] ascribe this to reversal of proton transfer in the initial decomposition step.

Bircumshaw and Newman [7] report that exposure to water vapor has a “rejuvenating” effect on partially-decomposed ammonium perchlorate. Samples which have undergone low-temperature decomposition through their deceleratory phase can decompose further after exposure to water vapor.

X. ROLE OF CRYSTAL DEFECTS

The importance of crystal defects in low-temperature decomposition is readily apparent from the inhomogeneous nature of the process: as discussed in the above sections, nucleation sites and pores form in localized regions of the crystal, with preference for certain crystallographic orientations.

Crystal defects in general fall into four categories: point defects (lattice vacancies, interstitial defects, substitutional defects, etc.), line defects (dislocations), planar defects (grain boundaries, stacking faults, and surfaces), and volume defects (voids, cracks, inclusions, and impurity clusters). Of these, dislocations, surfaces, and voids have been conclusively shown to play an important role in initiation of the decomposition process.

(i) Surfaces

Surfaces have at least two roles in the low-temperature decomposition process; they serve as a nucleation site for reaction centers during the induction phase and as a reaction site during the acceleratory phase.

As discussed above in Section V(i); the first physical evidence of decomposition is the formation of small pits on crystal surfaces [23-25]. Herley, Jacobs, and Levy [24] conducted an optical and electron microscopic study of nucleation in AP single crystals, in which strained and unstrained AP single crystals were heated briefly to induce decomposition. They observed nucleation sites to appear on certain faces (primarily the *c* and *m* faces in unstrained crystals) with alignments similar to etch pits generated by chemical etching. This suggests that the nucleation sites arise at points of intersection between surfaces and dislocations; chemical etching preferentially dissolves material in the vicinity of crystal defects and is a common technique for revealing the location and orientation of dislocations.

Surfaces have also been shown to participate in the acceleratory portion of the thermal decomposition process. Minier and Behrens [14], monitoring the temporal evolution of reaction products generated during decomposition of AP powders under various degrees of confinement, have demonstrated the existence of multiple reaction channels, some of which involve surface reactions. In order of temporal occurrence, these channels are: (*i*) one channel that involves reactions on the surface of the AP particles (main products $HClO_4$, HCl, O_2, and N_2O), (*ii*) one that consists primarily of decomposition within the solid (main products Cl_2, N_2O, H_2O, and O_2), and (*iii*) one that involves reaction between solid-phase decomposition products and the surface of the AP particles (products similar to channel *ii*, with abundant production of HCl). The dependence of the rates of formation of products on confinement and pressure, as well as differences in their product spectrum as compared to the second channel, indicates that channels (*i*) and (*iii*) involve surface reactions.

(ii) Dislocations

As discussed above, dislocations have been shown to be important in the nucleation process; nucleation appears to commence at the intersections between dislocations and crystal surfaces. Herley, Jacobs, and Levy [24] observed nucleation sites to appear on certain crystal faces with alignments similar to etch pits generated by chemical etching, suggesting that the nucleation sites arise at points of intersection between surfaces and dislocations. This is examined and analyzed in greater detail by Herley, Jacobs, and Levy in a subsequent publication [35]. Similar results were reported by Raevskii *et al.* [36].

(iii) Voids

Voids, which are empty spaces of microscopic dimensions within the interior of the crystal, have been shown to have an effect on the decomposition process by Minier and Behrens [14] in thermal decomposition experiments on AP powders. Minier and Behrens found that, during the initial stages of reaction, pores form on both exterior and interior surfaces of the powder particles, and proceed to propagate inward from the exterior surfaces of the particles and outward from the interior surfaces of voids. This suggests that the surfaces of voids play a role in the decomposition process similar to the external surfaces discussed above.

XI. PROPOSED THERMAL DECOMPOSITION MECHANISMS

A full mechanism for the low-temperature thermal decomposition of ammonium perchlorate must explain all of the experimental observations described in the above sections. Mechanisms have been proposed for each step of the decomposition process, as well as for the process as a whole. These mechanisms are reviewed here sequentially, starting with the initiation of decomposition at localized sites within the crystal.

(*i*) *Initiation of decomposition at localized sites*

The fact that the high-temperature decomposition process (>350°C) proceeds with no induction period and results in complete decomposition of the crystal suggests that the high-temperature mechanism involves direct breakup of the NH_4ClO_4 lattice. The low-temperature decomposition process (<300°C), in direct contrast, is anisotropic and incomplete: it begins at localized sites during a lengthy induction period and then proceeds into the crystal, ultimately leaving a stable residue of porous (but pure) NH_4ClO_4. This means that the low-temperature decomposition process must begin at crystal defects or impurity sites, where the barrier to reaction is lower than the perfect crystal, and initiate decomposition of the otherwise-stable surrounding lattice by some chemical and/or physical mechanism.

Two mechanisms have been proposed for this initiation step. Raevskii and Manelis [22] and Herley, Jacobs, and Levy [24,34] have argued that the reaction begins at points where dislocations intersect crystal surfaces. Herley, Jacobs, and Levy observed strong correspondence between the alignment of dislocations in the crystal, and the alignment of pits formed during the induction stage of the decomposition process, in both strained and unstrained single crystals. Both investigations noted similar densities of surface nuclei and dislocations; approximately $10^6/cm^2$. Both investigations argue that initiation of decomposition at the intersection of dislocations with the surface provides explanations for many phenomena observed during the induction period. Reaction at a dislocation site can potentially explain the anisotropy of the low-temperature decomposition process: the barrier to reaction at a dislocation can be lower than barrier to reaction in the perfect lattice, potentially allowing localized decomposition to occur, and reaction at a site where a dislocation intersects a surface provides a mechanism for the escape of gaseous reaction products and the formation of observed surface pits. As will be discussed in later sections, initiation of reaction at dislocation sites also suggests natural mechanisms for propagation of the reaction from the surface into the surrounding material.

Khairetdinov and Boldyrev [30] have argued that the reaction is initiated by the presence of chlorate (ClO_3^-) ions in the ammonium perchlorate lattice. The authors note that chlorate is present at low levels in samples of ammonium perchlorate, and show, using kinetic data, that increased chlorate concentration in ammonium perchlorate reduces the length of the induction period, and increases both the nucleation rate and total number of nucleation centers produced during the induction period. The authors argue that chlorate ions will be distributed unevenly throughout the crystal, preferentially accumulating at grain boundaries and dislocations, providing a mechanism to explain the initiation of reaction at localized sites.

(*ii*) *Chemical nature of initial reaction*

Electron transfer mechanism. Multiple mechanisms have been proposed for the initial reaction in the decomposition process. Bircumshaw and Newman [8] and Bircumshaw and Philips [12] initially proposed that the initial reaction involves the transfer of an electron from the ClO_4^- ion to the NH_4^+ ion, forming neutral NH_4 and ClO_4 radicals:

$$\mathrm{NH_4^+ClO_4^-} \rightarrow \mathrm{NH_4} + \mathrm{ClO_4}, \tag{2}$$

with subsequent reactions of NH_4 and ClO_4 ultimately leading to the observed stable decomposition products H_2O, O_2, Cl_2, N_2O, HCl, NO_2, N_2, (and others). The authors support this conclusion on the basis of their observations that (1) the addition of metal-containing compounds, such as MnO_2 and Fe_2O_3, shortens the induction period, and (2) ultraviolet irradiation experiments [12], which showed that the induction period shortens in response to irradiation by ultraviolet light. The authors argue that the shortening of the induction period by the addition of MnO_2 and Fe_2O_3 may be due to their ability to act as a bridge in electron transfer reactions, and that ultraviolet irradiation should affect the electronic structure of the solid rather than promote proton transfer reactions, which result in formation of NH_3 and $HClO_4$ and sublimation of the solid:

$$\mathrm{NH_4^+ClO_4^-} \rightarrow \mathrm{NH_3} + \mathrm{HClO_4}. \tag{3}$$

Proton transfer mechanism. Jacobs and Russell-Jones [37] and Davies, Jacobs, and Russell-Jones [27] subsequently argued that both sublimation and decomposition can be explained by a proton transfer mechanism:

$$\begin{array}{r}
\mathrm{NH_4^+ClO_4^-} \leftrightarrow \mathrm{NH_3 - H - ClO_4} \leftrightarrow \mathrm{NH_3 - HClO_4} \\
\updownarrow \qquad\qquad\qquad \\
\mathrm{NH_3}(ads) + \mathrm{HClO_4}(ads) \rightarrow products \\
\updownarrow \qquad\qquad\qquad \\
\mathrm{NH_3}\ (g) + \mathrm{HClO_4}(g) \rightarrow products
\end{array} \tag{4}$$

As the mechanism above suggests, proton transfer from NH_4^+ to ClO_4^- results in a neutral complex of NH_3 and $HClO_4$, initially adsorbed on the crystal, but free to escape the crystal as gaseous NH_3 and $HClO_4$. In this mechanism, reactions between NH_3 and $HClO_4$, either on the surface or in the gas phase, ultimately produce the stable decomposition products H_2O, O_2, Cl_2, N_2O, HCl, NO_2, N_2, and others; escape of NH_3 and $HClO_4$ without reaction concurrently explains the dissociative sublimation process. They argue that proton transfer is the key step that enables both decomposition and sublimation, having measured similar activation energies for both sublimation and decomposition (~30 kcal/mol). The suppression of decomposition by the presence of ammonia vapor would appear to support the proton transfer mechanism – the addition of ammonia gas would bind $HClO_4$, reforming NH_4ClO_4.

Chlorate decomposition mechanism. Khairetdinov and Boldyrev [30], who proposed that localized initiation proceeds at chlorate (ClO_3^-) impurity sites, suggest that the initial reactions may proceed as follows:

$$\begin{gathered}
\mathrm{NH_4^+ClO_4^-} \leftrightarrow \mathrm{NH_3} + \mathrm{HClO_4} \\
\mathrm{HClO_4} + \mathrm{ClO_3^-} \leftrightarrow \mathrm{ClO_4^-} + \mathrm{HClO_3} \\
\mathrm{HClO_3} \rightarrow \mathrm{ClO_2} + \mathrm{R}
\end{gathered} \tag{5}$$

with ClO_2 subsequently initiating decomposition of the surrounding ammonium perchlorate. Khairetdinov and Boldyrev support this reaction mechanism with the observations that (1) chlorate is an unavoidable impurity present in ammonium perchlorate, and the induction period of the decomposition process decreases with increasing chlorate impurity, (2) chloric acid,

$HClO_3$, is unstable under the conditions encountered in low-temperature decomposition, and decomposes to form, in part, ClO_2, (3) treatment of ammonium perchlorate with ClO_2 accelerates the decomposition process, and (4) ClO_2 is known to oxidize ammonia, producing $HClO_4$, which may then regenerate additional ClO_2.

While the suggestion by Jacobs and Russell-Jones [37] that proton transfer is the initial step in both decomposition and sublimation provides an elegant explanation for the parallel decomposition and dissociative sublimation reactions, and appears to be supported by measured activation energies, it must be stated that no direct measurement has confirmed or denied the above mechanisms; all have been supported by the indirect (but significant) observations described above. While the proton transfer mechanism appears to be most widely accepted in the literature (see discussion in Jacobs and Whitehead [1], Galwey and Mohamed [38,39], Minier and Behrens [13]), it is possible that multiple mechanisms are active in the decomposition process, particularly for metal-catalyzed decomposition. Further investigations are required to evaluate the above initiation mechanisms.

(*iii*) *Mechanism of propagation from surface into surrounding crystal*

The suggestion by Raevskii and Manelis [22] and Herley, Jacobs, and Levy [24] that nucleation may begin at the points of intersection between dislocations and the crystal surface naturally suggests a method of propagation into the surrounding crystal. The authors note that gaseous reaction products may accumulate in the vicinity of a decomposition site, locally straining the crystal, and generating new dislocations in the vicinity of the reacting nucleus [22], and perpetuating the decomposition process inward along the dislocation. Herley *et al.* [24] note that a screw dislocation in particular may provide a self-perpetuating nucleation site, as the surface step will be continually regenerated as the reaction propagates down the dislocation.

(*iv*) *Reaction mechanisms for decomposition within solid*

Electron transfer mechanism. According to the electron transfer mechanism proposed by Bircumshaw and Newman [8], the NH_4 radical produced by electron transfer first dissociates into NH_3 and a proton:

$$NH_4 \rightarrow NH_3 + H \tag{6}$$

The proton then reacts with ClO_4:

$$H + ClO_4 \rightarrow H_2O + ClO_3 \tag{7}$$

The ClO_3 so produced may subsequently decompose and/or react with NH_3 reacts to form the final decomposition products.

Proton transfer mechanism. Jacobs and Pearson [34], following Davies, Jacobs, and Russell-Jones [27], have proposed an extensive reaction mechanism for solid-phase decomposition based on the proton transfer mechanism. Proton transfer first generates NH_3 and $HClO_4$, and $HClO_4$ subsequently decomposes into reactive products that oxidize ammonia and undergo other secondary reactions:

$$\begin{gathered}
NH_4^+ClO_4^- \rightarrow NH_3 + HClO_4 \\
HClO_4 \rightarrow ClO + O_2 + OH \\
ClO + NH_3 \rightarrow NH_2 + ClOH \\
ClOH + OH \rightarrow H_2O + ClO \\
NH_2 + O_2 \rightarrow HNO + OH \\
HNO \rightarrow H + NO \\
HNO + OH \rightarrow NO + H_2O \\
NH_2 + NO \rightarrow N_2 + H + OH \\
HNO + HNO \rightarrow N_2O + H_2O \\
HNO + NO \rightarrow N_2O + OH \\
ClO + ClO \rightarrow 2Cl + O_2 \\
ClOH + Cl \rightarrow ClO + HCl
\end{gathered} \tag{8}$$

$$\begin{gathered}\mathrm{NO + ClO \rightarrow NO_2 + Cl}\\ \mathrm{Cl + Cl + M \rightarrow Cl_2 + M}\\ \mathrm{OH + OH \rightarrow H_2O + \tfrac{1}{2}O_2}\\ \mathrm{H + OH \rightarrow H_2O}\end{gathered}$$

Jacobs and Pearson also provide stoichiometric factors for each elementary reaction, which together reproduces the approximate product distribution observed in low-temperature decomposition:

$$\begin{aligned}\mathrm{NH_4ClO_4} &= 0.60\ \mathrm{O_2} + 0.07\ \mathrm{N_2} + 0.26\ \mathrm{N_2O} + 0.01\ \mathrm{NO} + 0.32\ \mathrm{NO_2}\\ &+0.24\ \mathrm{HCl} + 0.38\ \mathrm{Cl_2} + 1.88\ \mathrm{H_2O} \qquad (9)\end{aligned}$$

This mechanism is remarkable in that it provides a set of elementary reactions which together account for nearly all of the major products observed during low-temperature decomposition. The reaction mechanism does not, however, account for the formation of ClO_2, which as discussed above has been observed in multiple studies. Jacobs and Whitehead [1], in their review, discuss these elementary reactions in great detail.

Chlorate decomposition mechanism. Khairetdinov and Boldyrev [30], who proposed that reaction begins at chlorate impurity sites, suggest that $HClO_3$ reacts to produce ClO_2, which decomposes the surrounding ammonium perchlorate by oxidation of ammonia:

$$\begin{gathered}\mathrm{NH_4^+ClO_4^- \leftrightarrow NH_3 + HClO_4}\\ \mathrm{HClO_4 + ClO_3^- \leftrightarrow ClO_4^- + HClO_3}\\ \mathrm{HClO_3 \rightarrow ClO_2 + R}\\ \mathrm{ClO_2 + NH_3 \rightarrow HClO_4 + R}\end{gathered} \qquad (10)$$

The regeneration of perchloric acid and subsequent production of ClO_2 establishes a catalytic cycle.

Nitryl perchlorate mechanism. Galwey and Mohamed [38,39] have proposed that decomposition is promoted by the formation of an intermediate, nitryl perchlorate (NO_2ClO_4). In their experiments, they have determined that a small quantity of NO_2ClO_4 is present during decomposition, and argue that its formation and decomposition is the rate-controlling step in ammonium perchlorate decomposition based on the similar activation energies for low-temperature decomposition of ammonium perchlorate and pure nitryl perchlorate (~140 kJ/mol, or ~33 kcal/mol) [40], as well as the fact that the addition of a variety of nitrate additives (including NH_4NO_3) promote decomposition of ammonium perchlorate.

(*iv*) *Surface and gas-phase reactions*

Behrens and Minier [10] and Minier and Behrens [13,14] have shown that multiple branches exist in the decomposition mechanism, by comparing the rates of generation of gaseous products of low-temperature decomposition under vacuum and with the decomposition gases confined. They describe four separate reaction channels: (1) dissociative sublimation, to form gaseous NH_3 and $HClO_4$; (2) surface reactions between the decomposition gases and the solid ammonium perchlorate, whose rates increase with increasing pressure of decomposition gases; (3) decomposition within the solid ammonium perchlorate, with rate independent of external pressure; and (4) a reaction channel that appears to involve reactions among the gas-phase decomposition products and/or reactions of the decomposition products with the surface of the solid ammonium perchlorate. The solid-phase decomposition, surface reactions, and gas-phase reactions produce similar reaction products; the main difference is the relative production rates of decomposition species. These results highlight the fact that surface reactions and potentially gas-phase reactions are important as well.

(*v*) *Mechanism of propagation throughout solid and termination of reaction*

The results described in Section V clearly illustrate that decomposition progresses inward from the surface in single crystals of ammonium perchlorate, and simultaneously inward from the surface and outward from interior defects in ammonium perchlorate powders. Khairetdinov and Boldyrev [30], Galwey and Mohamed [39], and Minier and Behrens [13] have proposed similar physical mechanisms to account for the propagation of porosity throughout the solid and termination of the decomposition reaction.

Perchloric acid catalysis. Khairetdinov and Boldyrev [30] have proposed that reaction is initiated by decomposition of $HClO_3$ or ClO_3^- ions near the surface to produce ClO_2, which oxidizes ammonia, producing $HClO_4$ and H_2O. $HClO_4$ then decomposes to produce more ClO_2, resulting in a catalytic cycle. This catalytic cycle drives inward decomposition of the ammonium perchlorate, generating inward-moving pores. As water accumulates within the developing pore, Kairetdinov and Boldyrev argue that it tends to form perchloric acid hydrates; $HClO_4 \cdot H_2O$, $HClO_4 \cdot 2H_2O$, etc., which inhibit further decomposition. This produces a mechanism for limiting the size of the pores, which are observed to be approximately 2 μm in width. The high pressure generated within the reacting volume results in mechanical tension on the surrounding ammonium perchlorate which, combined with diffusion of ClO_2, allows further inward decomposition. Khairetdinov and Boldyrev also note that reaction within a pore near a surface can break the wall of the material, releasing decomposition gases and halting the reaction; this provides a mechanism for termination of reaction.

Nitryl perchlorate reacting fluid. Galwey and Mohamed [38,39] have proposed that the inward decomposition proceeds through the reaction of oxidized nitrogen with perchloric acid to produce NO_2ClO_4, which subsequently decomposes to ultimately generate the observed decomposition products. The authors postulate that, given the volatility of NO_2ClO_4 and the presence of other perchlorates in the reaction zone, NO_2ClO_4 decomposes in molten droplets, and the reaction progresses by an advancing zone of reacting fluid. Galwey and Mohamed note that NO_2ClO_2 can only participate in decomposition when it is retained within the reacting pores; depressurization of the pores (by interconnection of a pressurized and vented pore, for example) would lead to escape of the reacting fluid and termination of reaction.

Percolation theory treatment of decomposition. Erikson [41] has shown that the frational decomposition and evolution of porosity in the low-temperature decomposition process can be understood in the context of percolation theory. Erikson modeled the decomposition process using Monte-Carlo simulations, which divide the particle into discrete units, and propagates reaction by imposition of rules for reactions between adjacent units. The simulations assume that decomposition begins at chosen defect sites near the surface of the particles, can propagate to adjacent units, and halts when channels reach the surface of the particle and "vent". With these simple rules, the simulations show that decomposition tends to halt when around 30% of the particle is decomposed, and the extent of decomposition scales with particle size in agreement with experimental data. This supports the conclusions reached in previous investigations that decomposition results from reactions between pressurized gas within the developing pores and unreacted material, and halts when internal pressure is relieved.

(vi) Validity of proposed mechanisms

The above decomposition mechanisms are compelling, and provide a basis for understanding how decomposition of the solid is perpetuated. It must be noted, however, that many of these mechanisms have not been extensively supported by direct experimental evidence, due to the difficulties in performing *in situ* observations of intermediate species in the reacting sample. The implementation of a full kinetic model, including all elementary reactions, may hold the key to proving the importance of the above reaction mechanisms. It must also be noted that these mechanisms are not necessarily in conflict – multiple mechanisms may be simultaneously or sequentially active in solid-phase decomposition.

XII. CONCLUSIONS AND FUTURE WORK

This paper presents a review of previous work on the mechanism of low-temperature decomposition of ammonium perchlorate. The development of a comprehensive mechanism for low-temperature decomposition has been challenging, because the decomposition process is driven by a network of solid-phase, gas-phase, and surface reactions whose dynamics depend on physical properties such as particle size, exposed surfaces, and crystal defects.

Several aspects of the decomposition process are at this stage well-understood. It is well-understood that the decomposition process possesses three distinct phases; an induction phase during which internal decomposition begins, an acceleratory phase during which gas phase products are generated and the crystal becomes microporous, and a deceleratory phase during which decomposition ceases and remains incomplete. The spectrum of product gases is well-characterized, and includes H_2O, O_2, N_2O, Cl_2, N_2, NO_2, NO, HCl, ClO_2, NH_3 and $HClO_4$. Decomposition proceeds in parallel with dissociative sublimation. Decomposition begins, both in single crystals and in powders, near or just beneath exterior and interior surfaces, and proceeds outward from these sites. Chemical impurities and crystal defects have been shown to accelerate decomposition, ostensibly by providing nucleation sites and/or lowering energetic barriers to reaction.

At the same time, many features of the decomposition process remain incompletely understood. Chief among these are the nature of the initial reaction, the role(s) that various types of defects and impurities play in this initiation process, and the chemical reactions that proceed within the reacting solid. Future work is needed along these lines. At present, it is difficult to experimentally interrogate the localized chemistry that occurs at micro- and nanoscopic defect sites (such as dislocations) and within the pores of the reacting sample. In the near term, understanding of the decomposition mechanism may benefit from further study of crystal defects in ammonium perchlorate. Thermal decomposition studies that carefully control these factors will also be very informative. Computationally, multiscale methods may shed light on the microscopic events of the decomposition process that are as yet unobservable experimentally.

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