Photoproduction of disorder in $Pb(N_3)_2$ and TlN_3

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Azides of lead and thalium have been exposed to ultraviolet and x-ray irradiation, and the resulting changes in optical properties have been studied. These irradiations were found to produce a structureless increase in extinction, which increases in magnitude with decreasing wavelength to the band edge. Calculations indicate that the wavelength dependence of this irradiation-induced extinction is what might be expected from colloidal metal. The increased extinction is insensitive to the temperature of observations, and diffuse reflectance measurements indicate that some part, if not all of it, is due to absorption. Both of these results are to be expected if the extinction is due to colloidal metal. Essentially the same type of extinction is obtained for ultraviolet and x-ray irradiation at sample temperatures of 12, 78, and $\sim$ 300 K. Some differences between $Pb(N_3)_2$ and TlN_3 are discussed.

I. INTRODUCTION

The inorganic azides are very sensitive to various forms of radiation, including, ultraviolet light and x rays.[1] The azide ion, N_3^-, is a linear array of three nitrogens, which may dissociate upon electronic excitation. Many point imperfections have been detected in the alkali azides by electron-spin resonance. These have been produced by irradiation and include N^0, N_2^-, N_3^{--}, N_4^-, and the F center.[1-5] Many optical bands also are produced by irradiation; the spectra resemble those obtained from various kinds of glass and quartz and, to some extent, the alkali halides.[1,6-8] These optical bands suggest a variety of pointlike defects, and there has been some success at correlating the bands with the defects detected by electron-spin resonance, e.g., the N_4^-.[8]

In contrast to the alkali azides, the heavier-metal azides, PbN_6, TlN_3, and AgN_3, do not show evidences of pointlike defects on irradiation.[9-11] No molecular defects have been observed in these azides by spin resonance, and the optical spectra exhibit very little structure. $Ba(N_3)_2$ may be an intermediate case since it exhibits some properties of both of these groups of azides. Thus molecular defects have been observed by spin resonance in this azide,[2,12] but the optical properties following irradiation more nearly resemble those of the heavier metal azides.[9,10] However, all of these azides, within the room-temperature range, evolve nitrogen gas on irradiation and so decompose under the influence of radiation.[1] The work reported in this paper is concerned with the disorder generated in the heavy-metal azides, PbN_6 and TlN_3, as a result of irradiation.

II. EXPERIMENTAL

Samples for optical measurements were grown from solution; e.g., $Pb(N_3)_2$ was grown from a saturated solution of ammonium acetate by slow cooling.[13] Visual and optical observations indicate reasonably good but small single crystals. TlN_3 samples were grown from aqueous solutions by evaporation. The samples were in general small, polycrystalline, and not clear. The small size of both $Pb(N_3)_2$ and TlN_3 samples and the light scattering properties of TlN_3, which were most probably due to internal boundaries, made optical measurements rather difficult and decreased their precision considerably. The samples were approximately $3\times2\times1$ mm.

Samples were exposed either to ultraviolet light or to x rays. The ultraviolet light was obtained from a high-pressure Hg lamp, and filters were used to give primarily the 3650-Å line. In a few cases, samples were exposed to unfiltered light from the Hg source or from the ir #2 tungsten lamp source of the Cary spectrometer. x rays were obtained from a source operating at 30 kV (peak) and 20 mA or another source operating at 50 kV (peak) and 40 mA. An Al filter was used to remove the softer x rays from the beam.

For irradiation and measurement at low temperatures samples were mounted in a standard vacuum cryostat manufactured by Sulfrian Cryogenics, Inc. For measurements at room temperature samples were mounted either in the vacuum cryostat or in air. Temperature measurements were made using a platinum resistor and a resistance bridge. The platinum resistor was secured to a copper block which served as a base for attaching the sample holder. All temperatures reported are those of the platinum resistor. In addition, the term "300 K" is used very loosely to mean room temperature. This temperature was in many cases unmeasured. For mounting in the cryostat the sample was glued with Duco cement to a copper plate (sample holder) which was bolted onto the copper block. Optical absorption measurements were made with a Cary spectrophotometer, Model No. 14R, and diffuse-reflectance measurements

with a Perkin-Elmer spectrophotometer, Model No. 350. It is important to note that attenuation of the beam on passing through a sample can be due to absorption and/or scattering, and the term extinction includes both. Because of the high-absorption coefficient of the samples for x rays and ultraviolet light, defects are not produced throughout the whole volume of the sample. Thus it is not easily possible, even in cases where the extinction is due only to absorption, to convert optical density into an absorption coefficient.

III. RESULTS

A. Irradiation-induced changes in optical transmission

In Fig. 1 typical results are given for $Pb(N_3)_2$.[9,10] The abrupt increase in optical density at about 4050 Å is due to the absorption edge. Figure 1 indicates that exposure to the output of an unfiltered W lamp causes a structureless change in extinction which increases monotonically with decreasing λ from the red to the blue. Similar results are obtained for other forms of radiation. In Fig. 2 results are given for a TlN_3 sample which has received a prolonged exposure to x rays. Similar results have been obtained for $Pb(N_3)_2$. The data of Fig. 2 are presented to show that the structureless increase in extinction extends into the infrared.

The data presented in Fig. 3 indicate that essentially the same results are obtained when $Pb(N_3)_2$ is exposed to ultraviolet light at 12, 78, or 300 K. Similar results are obtained for x-ray irradiation at 78 and 300 K. The data for this figure were chosen to have approximately the same optical density at each temperature so that comparisons could easily be made. The irradiation dose is not the same in each case. Most of the differences in the curves of Fig. 3 are within the range of variations from sample to sample and even from measurement to measurement on the same sample. Examination with a low-power microscope reveals that the samples are not uniformly colored. This nonuniformity of coloration, coupled with the small sample size and the difficulty of reproducing the exact position of the sample in the spectrophotometer beam, most probably accounts for most of the differences between the curves in Fig. 3. In addition, scattering from small surface and volume irregularities further causes the results to be very sensitive to the position of the sample in the spectrophotometer beam. Some of the differences between these curves may, however, be significant, and this problem is considered further below.

When TlN_3 is exposed to ultraviolet light at 12, 80, and 300 K the results are similar to those given in Fig. 3. In addition, there is little difference in the results for TlN_3 exposed to ultraviolet light or x rays at 300 K. However, when TlN_3 is exposed to x rays at 80 K, the effect is somewhat

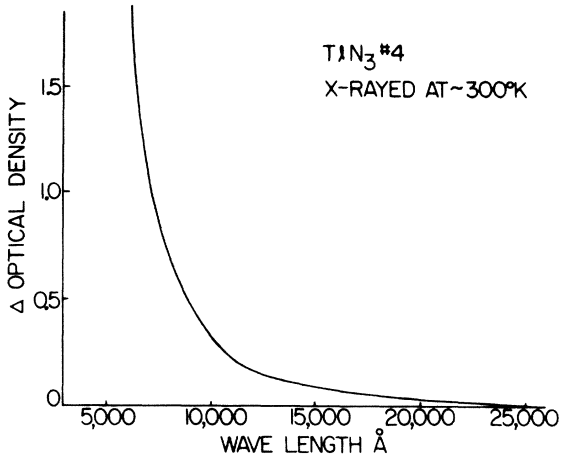

FIG. 2. Change in optical density vs wavelength for x-irradiated TlN_3.

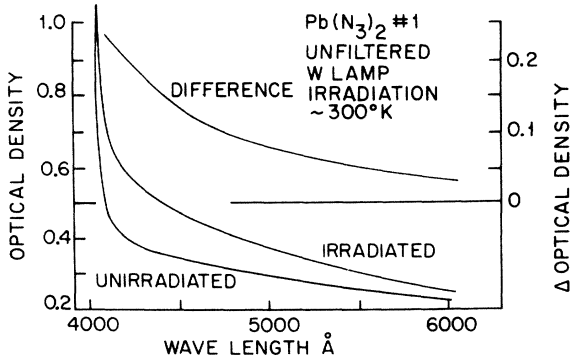

FIG. 1. Optical density of unirradiated and irradiated $Pb(N_3)_2$ vs wavelength λ. The difference in optical density is also given vs λ.

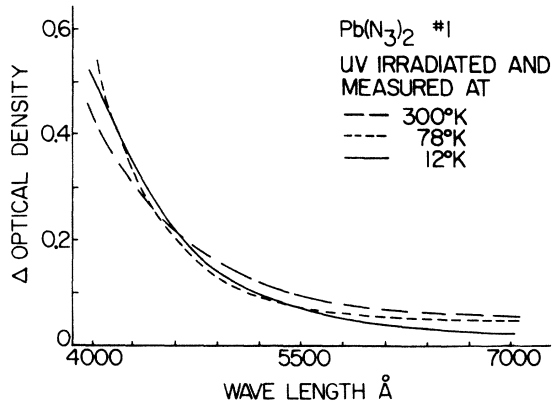

FIG. 3. Change in optical density vs wavelength due to ultraviolet irradiation of $Pb(N_3)_2$ as a function of sample temperature during irradiation.

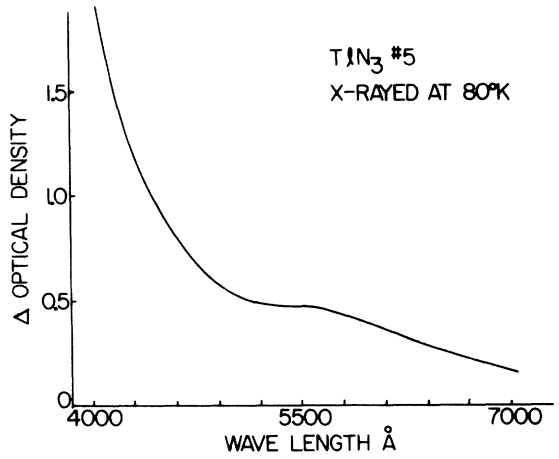

FIG. 4. Change in optical density of TlN_3 due to x irradiation at 80 K.

different, as shown in Fig. 4. In this case there is a weak band at about 5500 Å superimposed on the structureless change in optical density characteristic of other conditons. This band at about 5500 Å anneals on warming to 300 K, and suggests that presence of point defects due to irradiation.

B. Colloidal metal considerations

As noted in the Introduction, lead and thallous azides evolve nitrogen gas when exposed to ultraviolet light at temperatures in the vicinity of room temperature.[1] In this investigation it has been found that gas, presumably nitrogen, is given off when TlN_3 is exposed while at temperatures slightly above that of liquid nitrogen. These facts, plus the lack of evidence for point defects under most conditions as a result of irradiation, suggest that colloidal metal may be formed during irradiation, as is the case in the silver halides,[14] and as has been suggested for silver azide.[11] Thus the change in optical density may be due to colloids. Calculations of the absorption due to colloidal Pb and Tl have recently been carried out by M. Barkey and T. Gora of this Laboratory.[15] They have used the Mie Theory for a low density of small (diameter < 250 Å) spherical particles. The results for Pb (Fig. 5) indicate a structureless absorption which increases in going from long to short wavelength, in general agreement with experiment. These calculations do show a plateau at longer wave lengths which is not observed experimentally. The results of calculations for Tl are very similar to the Pb results (Fig. 5).

The optical constants for $Pb(N_3)_2$ and TlN_3 are not available, so that the calculations are for Pb and Tl in matrices of material having a few arbitrarily chosen values of the index of refraction, which do not vary with λ. Since the observations are in the vicinity of the absorption edge, the optical constants will in fact be wavelength dependent. The calculations of Barkey and Gora do, however, indicate that the observed changes in extinction may be due to colloidal metal. It then is possible that some of the differences in the curves of Fig. 3 may be due to differences in the shape and size of colloidal particles.[16] It also is quite possible that the particle size, in particular, may depend on sample temperature during exposure and also on the density of ionization produced during irradiation. Since the absorption coefficients for ultraviolet light and for x rays are markedly different, the resultant densities of ionization also are considerably different. The mechanism for the production of colloidal metal during irradiation is not clear, especially at low temperatures where diffusion is not expected to be possible.

It is interesting to consider the optical properties of colloidal metal in addition to those already discussed. The extinction due to colloidal metal should be insensitive to the measurement temperature.[17] In Fig. 6 the optical density of a TlN_3 sample irradiated at 80 K is given for measurements at 80 and 300 K. The sample was heated to 300 K for measurement after exposure, and then recooled to 80 K for another measurement. Thus, any possible annealing effects caused by the first heating have been eliminated. It is clear that the extinction is insensitive to temperature, as expected for colloidal metal. Similar results have been obtained for $Pb(N_3)_2$.

The extinction due to colloidal metal should be composed of a component due to absorption and a component due to scattering,[16] and the importance of the scattering component will depend on particle size. In addition, inclusions of nitrogen could be expected to cause scattering, but no appreciable absorption.[16] Since nitrogen is known to escape

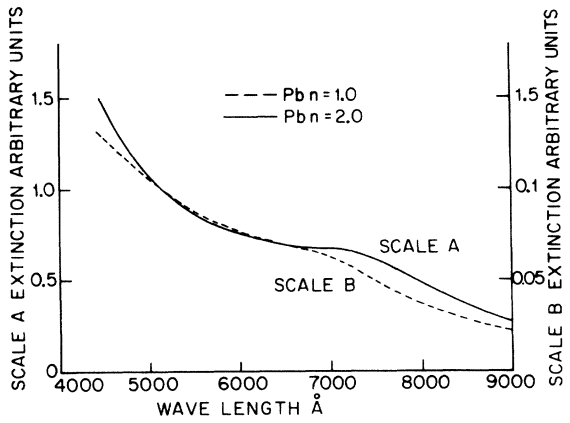

FIG. 5. Calculated extinction in arbitrary units vs wavelength for colloidal Pb as a function of the index of refraction of the surrounding material.

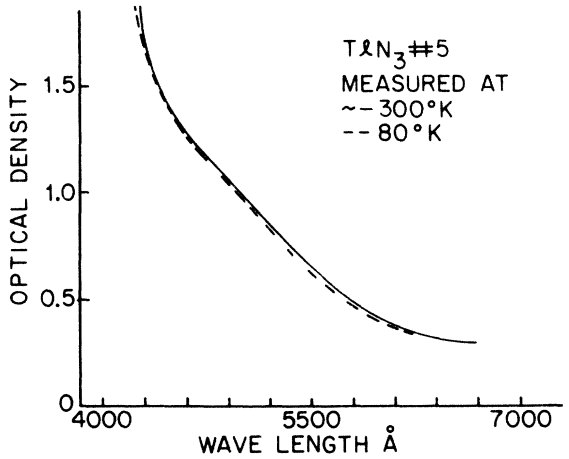

FIG. 6. Optical density vs wavelength for TlN_3 irradiated at 80 K. Measurements at 300 and 80 K.

during irradiation, it is not unreasonable to expect inclusions or bubbles of gas in the sample. Thus an extinction which is due largely to scattering suggests inclusions of nitrogen, while extinction which has a significant component due to absorption will support the hypothesis that it is due to colloidal metal. In the latter case, a comparison of the relative magnitudes of the scattering and absorption components may give information about the particle size. In an effort to determine whether or not a component of the extinction is due to absorption, measurements were made of changes in the diffuse reflectance due to irradiation. Powdered samples were used, and the diffusely reflected light was collected by an integrating sphere.

Results of diffuse reflectance measurements on unirradiated and irradiated TlN_3 are given in Fig. 7. This type of measurement does not distinguish between the scattering of light by imperfections and diffuse reflections, since the scattered light is collected by the integrating sphere independently of whether it is diffusely reflected or scattered by imperfections. However, energy which is absorbed by the powder is not collected by the sphere. The relationship between the diffuse reflection and the absorption coefficient is not simple, but it is monotonic,[18] and a decrease in diffuse reflectance indicates an increase in absorption. The sharp decrease in diffuse reflectance (Fig. 7) of the unirradiated material at about 4300 Å is due to the fundamental absorption edge. The data of Fig. 7 show that there is a structureless *decrease* in diffuse reflectance of the irradiated material which increases in magnitude on going from long to short wavelength. Thus there is a structureless *increase* in absorption due to irradiation which increases on going from the long to short λ. Hence the increase in absorption coefficient due to irradiation is, in wavelength dependence, very similar to the increase in extinction. From these measurements it is possible to conclude that part of the change in extinction is due to a change in absorption. This conclusion supports the hypothesis that colloidal metal is produced by irradiation. Additional measurements are necessary to determine if a significant part of the extinction is due to scattering.

C. Efficiency of defect production

The rate of defect production in $Pb(N_3)_2$ was studied as a function of temperature for ultraviolet light and for x rays.[19,20] The data show that the efficiency of defect production for ultraviolet irradiation decreases appreciably on going from 300 K to 78 K, while there is essentially no change in this efficiency for x-ray irradiation and the same temperature change. In addition, the data for ultraviolet irradiation show saturation characteristics with irradiation time, while the growth is linear for x-ray irradiation. These differences may be due to the difference in ionization density produced by the two types of irradiation. For ultraviolet irradiation the energy is absorbed in a thin surface layer, and in this surface layer the density of imperfections should be much higher than for x-ray irradiation. Thus the saturation character of the growth curves for ultraviolet radiation may be due to the fact that the sites at which the disorder is produced and/or stabilized are appreciably used up. Alternately, back reactions which are ionization-density dependent may account for the differences between the two types of radiation. For ultraviolet irradiation it is also necessary to consider the fact that the defects themselves absorb in the wavelength region of the damaging radiation and thus decrease the energy available for defect production. However, this is also the case for x-ray irradiation. Little change has been observed in the defect production efficiency on cooling from 78 K to 12 K for ultraviolet irradiation. While de-

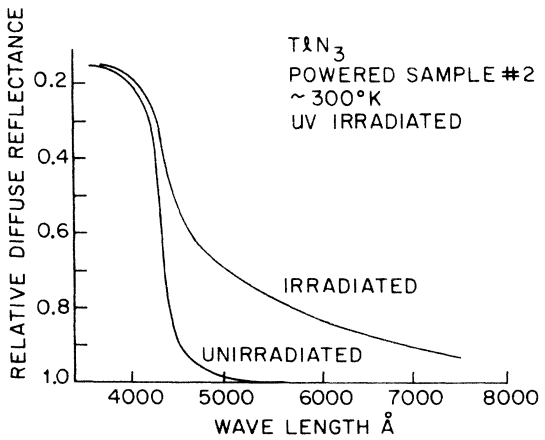

FIG. 7. Diffuse reflectance vs wavelength for powdered TlN_3.

tailed data are not available for TlN_3, it has been observed that the efficiency of defect production decreases with decreasing temperature for ultraviolet irradiation. The difference in the temperature dependence of colloidal metal production by x rays and ultraviolet light suggests that the latter produces bound excited states which require thermal activation to produce dissociation leading to decomposition. In contrast the higher-energy x rays may produce the dissociated state directly and thus eliminate the need for thermal activation. The kinetics of colloidal metal formation will be discussed more fully in a subsequent paper.

D. Annealing

When TlN_3 is irradiated at low temperature and then heated to room temperature, the only change in the optical density is due to the annealing of the small band at ~5500 Å for x-ray irradiation.[19,21] There is no change for ultraviolet irradiation. In contrast, if $Pb(N_3)_2$ is irradiated at a low temperature with ultraviolet light and heated to room temperature, essentially all of the induced change in extinction is annealed out in two or more annealing stages.[19,21] One of these stages is in the vicinity of 78 K. Thus in $Pb(N_3)_2$ it apparently is possible to disperse the colloidal metal by thermal treatment if the irradiation has been carried out at low temperatures.

E. Thermal decomposition

This work is primarily concerned with disorder produced by irradiation. However, essentially the same wavelength dependence of the change in optical density can be produced by heat treatment of TlN_3.[19] Thus, colloidal metal also may be produced during thermal decomposition. This conclusion is not surprising in view of the fact that nitrogen gas is also given off during thermal decomposition.[1]

IV. SUMMARY AND DISCUSSION

The results to date support the hypothesis that the structureless increase in optical extinction due to irradiation of $Pb(N_3)_2$ and TlN_3 is attributable, at least in part, to colloidal metal. The calculations of Barkey and Gora give results which are consistent with experiment; the extinction is insensitive to temperature as expected for colloids; and, finally, the diffuse-reflectance measurements show that at least part of the extinction is due to absorption. It is not possible at this time, however, to rule out the possibility that some part of the extinction is due to scattering from "colloidal" nitrogen or from compounds of nitrogen. To investigate this question, it will first be necessary to determine if a significant part of the extinction is due to scattering. If these additional experiments show that the extinction is exclusively due to absorption, it will be possible to rule out nitrogen or nitrogen compounds, since these are not expected to give appreciable absorption in comparison with scattering. It then may also be possible to place an upper limit on the colloidal metal particle size.[16] If, on the other hand, an appreciable component of the extinction is found to be due to scattering, it will be necessary to use other approaches to distinguish between colloidal metal and nitrogen. The calculations will be further pursued in an effort to better characterize what might be expected from various types of colloids.

A preliminary but unsuccessful search has been made for the spin resonance of conduction-band electrons in colloidal metal in irradiated TlN_3. The work to date is not complete and further experiments will be carried out. A conduction electron spin-resonance signal which is correlated with the optical results gives one of the most convincing arguments for the presence of colloidal metal.[22,23] There are, however, reasons why a signal may not be observed even in the presence of colloidal metal.

One of the most interesting parts of this work arises out of the possibility of colloid production at low temperatures, e.g., 78 and 12 K, due to exposure to radiation. Diffusion of the type necessary to produce colloids is generally not observed and not expected in nonmetallic systems at these low temperatures. While colloidal metal is produced in the silver halides and, in some cases, in the alkali halides by irradiation, in the vicinity of room temperature it is not produced, or at least not very efficiently produced, at low temperatures. A minimum condition for metal-colloid production might be that metal atoms or ions must be able to move over short distances, e.g., a few lattice parameters, so as to cluster. The necessary diffusion may take place only during irradiation if, for example, the charged state of the metal or nitrogen which diffuses exists only in the presence of radiation.

The observation that the coloration is nonuniform across the sample strongly indicates that the mechanism of disorder production is very sensitive to sample perfection. The process may be sensitized by chemical or mechanical imperfections as is the case in the silver halides.[14] Imperfections may act as nucleation centers for colloid production, or they may simply influence the trapping and the lifetimes of electrons, holes, and excitons, and so affect the efficiency of other processes which are dependent on the presence of these electronically excited states. The efficiency of defect production in alkali halides is strongly dependent on chemical and mechanical perfection.[17,24] Unfortunately, nothing is known about the intrinsic disorder in any

of the azides, and very little about diffusion. Diffusion is important in the photographic process, i.e., in the formation of colloidal silver during irradiation of the silver halides[14] and may be important in the formation of colloidal metal in the heavy-metal azides. In addition, the type of disorder produced by irradiation may at least in part be determined by the type of intrinsic disorder, e.g., the role of interstitial silver (an intrinsic defect in the silver halides) in the formation of colloidal silver.[14] In this respect it would be very helpful to know if interstitial metal is an intrinsic form of disorder in the heavy-metal azides. The nonisotropic nature of the azides may also influence the production and stability of imperfections.

Sharma has suggested that in TlN_3 fluorescence is a competing process with photodecomposition.[25] He has observed that there is a correlation between the magnitude of the fluorescence and the amount of photodecomposition, the fluorescence increasing with decreasing temperature, while the photodecomposition efficiency decreases with decreasing temperature. Further experiments are necessary to determine if a detailed correlation does exist between the fluorescence efficiency and the efficiency of photodecomposition.

Photodecomposition studies have also been made on thin films of $Pb(N_3)_2$ in wavelength regions of high-extinction coefficient which are not easily accessible using transmission techniques and single crystals.[26-28] It is pertinent to briefly discuss the results and conclusions of these workers in relationship to the work reported here. A maximum in the extinction coefficient at about 3750 Å is removed by ultraviolet exposure and upon further exposure the extinction coefficient in the region 3400 to 4000 Å increases and takes on the character of an exponential Urbach tail.[28] From these results and from loss of structure in the infrared extinction, it was concluded that the products of partial photocomposition are amorphous.[28] The increase in the extinction in the 3400 to 4000 Å range could be due to colloidal Pb, as reported in this work, possibly in amourphous form.

It is interesting to note that the thin films often apparently contain considerable disorder before irradiation as indicated by the optical extinction in the visible part of the spectrum (compare Fig. 1 or Ref. 26 and Fig. 3 or Ref. 29 with Fig. 1 in this paper for unirradiated material.) This extinction is due to scattering and not absorption since it is not observed in diffuse reflectance[29] and may be due to a variety of imperfections and/or sample inhomogeneities. Although the wavelength dependence of this scattering is similar to that reported in this paper for colloidal Pb in irradiated single crystals of $Pb(N_3)_2$, it is improbable that it is due to small particles of metallic Pb (colloidal Pb) not converted to $Pb(N_3)_2$ during the film-formation process because of the lack of absorption. Scattering from small clusters of Pb atoms not of sufficient size to have metallic absorption characteristics cannot be ruled out at this time.

Williams and co-workers[26-28] and Garrett[30] have also studied the evolution of nitrogen gas from $Pb(N_3)_2$ during photodecomposition for thin films and single crystals, respectively, and the general features such as wavelength dependence and quantum efficiency are similar for the two types of samples. A study of the relationship of the decomposition of the azide sublattice to that of the metal sublattice will be published elsewhere.[31]

Finally, it is interesting to speculate on a possible use of materials which are photosensitive at low temperatures. Preliminary experiments with powders indicate that both TlN_3 and AgN_3 are more photosensitive than AgCl at 80 K. It might therefore be useful to consider the possibility of employing either TlN_3 or AgN_3 as the photosensitive component of an emulsion to be used at low temperatures.[32] For either of these materials to be of practical use in this respect it will most probably be necessary to find some means of "developing," since the high efficiency of the silver halides arises because of the developing process.[14]

Note added in proof: Since this work was completed the author has become aware that J. Roth has obtained results for $Pb(N_3)_2$ exposed to sunlight which are similar to the results of Fig. 7 for TlN_3 [J. Chem. Phys. 41, 1929 (1964)].

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